mates that of the disk-coil model. It is interesting to note that the flexible coil value of [η] 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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[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.

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TABLE II

DIELECTRIC CONSTANTS, INTRINSIC VISCOSITIES, AND INTRINSIC VISCOSITY RATIOS AT 25°

Solvent	ϵ	$[\eta]_{16}$ ± S.D., ml g^{-1}	$[\eta]_2$ ± S.D., ml g^{-1}	$[\eta]_{16}/[\eta]_2$
6 *M* urea	92	5.36 ± 0.064	3.41 ± 0.063	1.57 ± 0.05
Water	78.5	5.52 ± 0.028	3.48 ± 0.020	1.59 ± 0.02
DMSO	45	3.36 ± 0.023	2.01 ± 0.013	1.67 ± 0.02
Methanol	32.6	4.07 ± 0.019	2.46 ± 0.007	1.65 ± 0.02
THP	7.4[a]	4.02 ± 0.013	1.87 ± 0.015	2.15 ± 0.03
Benzene	2.27	3.63 ± 0.018	1.47 ± 0.017	2.47 ± 0.05

[a] ϵ of tetrahydrofuran.

Results

The apparent specific volume data are summarized in Table I. The values in methanol and benzene are within 1% of the partial specific volumes obtained by Moacanin[6] for dipropylene glycol and PPG 2025 in the same solvents, and at similar concentrations.

The intrinsic viscosities of dipropylene glycol, $[\eta]_2$, and PPG 1025, $[\eta]_{16}$, are given in Table II together with the standard deviations, S.D. The results in water from the previous paper[1] are included for comparison. Also listed are the intrinsic viscosity ratios $[\eta]_{16}/[\eta]_2$, with their estimated uncertainty limits, and the dielectric constants of the solvents, ϵ. Examples of reduced viscosity–concentration plots are shown in Figure 1.

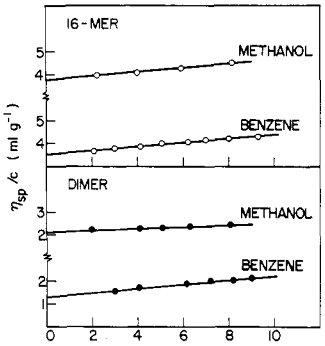

Figure 1. Reduced viscosity curves for the dimer and 16-mer in methanol and benzene.

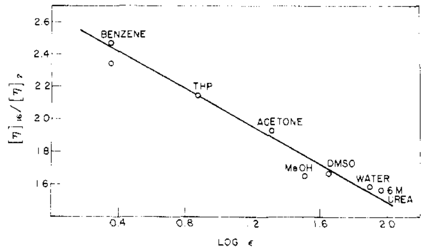

Figure 2. The dependence of the relative expansion of the 16-mer chain on the dielectric constant of the solvent.

Scholtan and Lie[7] determined the intrinsic viscosities at 20° in methanol, tetrahydrofuran, and benzene, of a polypropylene glycol sample of similar number average molecular weight as the 16-mer. Their intrinsic viscosities worked out to be 11% lower in methanol and 21% lower in benzene than the values in Table II. Their result in tetrahydrofuran was 4% greater than ours in tetrahydropyran. The intrinsic viscosity of PPG 1025 in benzene, 3.63 ml g^{-1}, falls between two other literature values at 25°, *viz.* 3.5 ml g^{-1} [8] and 3.76 ml g^{-1}.[9] For dipropylene glycol in benzene, we obtain an intrinsic viscosity of 1.47 ml g^{-1}. Other values which have been reported are 1.60 ml g^{-1} [9] and 1.25 ml g^{-1}.[6] Moacanin also reported an intrinsic viscosity of 2.12 ml g^{-1} for dipropylene glycol in methanol at 25°.[6] This may be compared with our own value of 2.46 ml g^{-1}.

From the above comparison, the average deviation between the data in Table II and results reported in the literature seems to be about ±0.2 ml g^{-1} in $[\eta]$. This is considerably higher than the standard deviations shown in Table II, and probably reflects the experimental difficulty in measuring intrinsic viscosities for chains of such low molecular weight.

Discussion

The conformational behavior of the polypropylene glycol oligomers in the various solvents can be related to the polar character of the solvent. Figure 2 shows a plot of $[\eta]_{16}/[\eta]_2$ *vs.* the logarithm of the solvent dielectric constant. The additional values of the ratios in benzene (2.35) and in acetone (1.93) were derived from the data of Meyerhoff, *et al.*[9] As the dielectric constant decreases the solvent becomes more hydrophobic and provides a more suitable van der Waals environment for the side-chain methyl groups. The improved solvent–solute interaction induces an expansion of the 16-mer chain which is reflected in a higher intrinsic viscosity ratio. Benzene is the most hydrophobic solvent, and from its high ratio it may be considered as the best "denaturant" for the propylene glycol chain.

The behavior of the aqueous urea system fits in well with the above argument. Urea actually raises the dielectric constant of water,[10] which leads to the lowest intrinsic viscosity ratio in the group. This result provides the interesting implication that urea cannot effectively break hydrophobic bonds in the propylene glycol oligomers, a conclusion which seemingly does not conform to current thinking: *viz.*, hydrophobic

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(8) J. Moacanin, *J. Appl. Polym. Sci*, **1**, 272 (1959).

(9) G. Meyerhoff and U. Moritz, *Makromol. Chem.* **109**, 143. (1967).

(10) International Critical Tables, Vol. 6, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p 100.

TABLE III

INTRINSIC VISCOSITY RATIOS FOR LINEAR POLYMER SYSTEMS

Polymer–solvent system	$[\eta]_{16}/[\eta]_2$	Ref
Polystyrene–toluene	2.6	*a*
Polyisobutylene–diisobutylene	2.8	*a*
Poly-α-methylstyrene–toluene	2.9	*b*
Polyhexamethylene oxide–dioxane	2.5	*c*
Polyhexamethylene oxide–benzene	2.7	*c*

[a] U. Bianchi and A. Peterlin, *J. Polym. Sci., Part A-2*, **6**, 1759 (1968). Extrapolations for these systems were made from enlarged drawings of the log $[\eta]$ − log M plots, kindly supplied by Professor Peterlin. [b] B. J. Cottam, J. M. G. Cowie, and S. Bywater, *Makromol. Chem.*, *86*, 116 (1965). [c] K. Yamamoto and H. Fujita, *Polymer*, *7*, 557 (1966).

bonds are disrupted in aqueous urea solutions.[2] In a recent ultrasonic attenuation study, Hammes and Roberts found that urea could give rise to a cooperative transition in aqueous polyethylene glycol–urea solutions which involved the weakening of intramolecular hydrophobic interactions in the polymer.[11] Significantly, however, these transitions did not occur at polymer molecular weights below 3400, a value which is about three times as great as that of our 16-mer. Thus, the results of Hammes and Roberts also suggest that aqueous urea does not break hydrophobic bonds in low molecular weight polyglycols.

It is of interest to compare the intrinsic viscosity ratios for the oligomeric propylene glycols with the values for some typical linear chains as listed in Table III. To obtain these ratios, the intrinsic viscosities at two molecular sizes were determined from the log $[\eta]$ − log M plots of several low molecular weight polymer systems. The intrinsic viscosity at one size, $[\eta]_2$, corresponded to the propylene glycol dimer with seven chain atoms and the intrinsic viscosity at the other size, $[\eta]_{16}$, corresponded to the 16-mer with 49 chain atoms. For the polystyrene, polyisobutylene, and poly-α-methylstyrene systems, the intrinsic viscosity for seven chain atoms was obtained by extrapolation of the linear log $[\eta]$ − log M plots to molecular weights of 364, 196, and 413, respectively. The extrapolations were not unduly long since the experimental molecular weight ranges for these systems extended down to 600 for polystyrene,[12] 650 for polyisobutylene,[12] and 1000 for poly-α-methylstyrene.[13] Values of $[\eta]_2$ for polyhexamethylene oxide[14] and of $[\eta]_{16}$ in all cases were obtained by interpolation of the $[\eta]$ − M data in the low molecular weight range.

It is likely that the linear polymers in Table III corresponding to the 16-mer with 49 chain atoms adopt a conformation in solution which is approximately that of a random coil.[12,13,15] As shown in Table III the range of viscosity ratios estimated for the linear polymers is from 2.5 to 2.9. Thus, polypropylene glycol in benzene, with a ratio of about 2.5, may be considered to fall into this class. The considerably lower value of 1.6 for polypropylene glycols in water supports a more compact conformation, such as the disk-coil, for the 16-mer in aqueous media.

The correlation of molecular conformation with the dielectric constant of the solvent is supported to some extent by the diffusion and viscosity measurements of other workers.[7,9,16] For molecular weights greater than 500, polypropylene glycol (PPG) in benzene assumes a random coil configuration, as indicated by the linear log $[\eta]$ *vs.* log M relationship with a slope of 0.65. Below this "critical" molecular weight the slope tends to zero. Meyerhoff, *et al.*,[9] attributed such behavior to a configurational change from a random coil to a "rotation ellipsoid" shape as the molecular weight decreased. These workers found that the corresponding "critical" molecular weight in acetone (ϵ = 20.7) was 1000. Thus, from their data it can be inferred that the 16-mer (mol wt $\simeq$1000) is randomly coiled in benzene and is in a transition state between the random coil and a more compact conformation in acetone, in good agreement with our present interpretation of the trend shown in Figure 2.

Similar behavior has been observed in the polyethylene glycol–water system. At high molecular weights the intrinsic viscosity behavior of polyethylene glycol (PEG) in water is typical of a random coil polymer in a good solvent. However, at a "critical" molecular weight of 3000, the exponent "*a*" in the Mark–Houwink equation undergoes an abrupt decrease from 0.78 to 0.287.[17] This latter value of "*a*" is well below the range expected for Gaussian behavior (a = 0.5 for a Gaussian coil under θ conditions) and it indicates that the oligomeric ethylene glycol chain in water assumes a configuration which is more compact than a random coil. However, it is unlikely that the PEG oligomer chain is as tightly coiled as PPG in water. PEG is relatively hydrophilic[18] and lacks the pendant methyl groups which enhance intramolecular hydrophobic bonding in the PPG oligomers. The tighter coiling of PPG in aqueous solution is borne out by the lower value of 1.6 for $[\eta]_{16}/[\eta]_2$, compared with a value of 1.8 determined for the PEG chain in water.[19]

The interpretation of the data in the above manner must be made with certain reservations, because of the fact that the intrinsic viscosities of the dimer in DMSO, THP, and benzene are less than the Einstein minimum value of 2.5 v. At present there is much uncertainty as to the theoretical meaning of such low intrinsic viscosities. Bianchi and Peterlin[12] have proposed that the viscosity behavior of oligomeric chains is, in large measure, dependent on the contribution made by the monomer unit. The validity of our interpretation rests on the assumption that specific solvent interactions with the monomer unit are the same in the dimer and in the 16-mer. Since shielding effects in these low D.P. oligomers are expected to be negligible, it seems reasonable to assume that the hydrodynamic

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(11) G. G. Hammes and P. B. Roberts, *J. Amer. Chem. Soc.*, **90**, 7119 (1968).

(12) See Table III, footnote *a*.

(13) See Table III, footnote *b*.

(14) See Table III, footnote *c*.

(15) C. Rossi, U. Bianchi, and E. Bianchi, *Makromol. Chem.*, **41**, 31 (1960).

(16) G. Meyerhoff, *Makromol. Chem.*, **107**, 124 (1967).

(17) J. A. Faucher and R. W. Callard in "Encyclopedia of Polymer Science and Technology," Vol. 6, Interscience Publishers, New York, N. Y., 1967, pp 128–131.

(18) F. E. Bailey, Jr., and R. W. Callard, *J. Appl. Polym. Sci.*, **1**, 56 (1959).

(19) H. G. Elias, *Makromol. Chem.*, **103**, 214 (1967).

perturbation produced by the individual bead is the same in both chains. Some support for this argument is provided by the fact that the intrinsic viscosities of the dimer and the 16-mer both tend to be low or high in the same solvents (*e.g.*, low in DMSO, THP, and methanol and high in water and 6 *M* urea), indicating that the solvent–solute interactions are similar for the short and the long chain. Thus although the absolute level of intrinsic viscosity may be difficult to interpret in terms of the hydrodynamic specific volume of the oligomer, the ratio $[\eta]_{16}/[\eta]_2$ may be taken as a measure of the relative chain expansion in a given solvent.

Viscoelastic Properties of Comb-Shaped Polystyrenes

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ABSTRACT: Comb-shaped polystyrenes having various numbers of branches and various molecular weights of a branch were prepared by an anionic polymerization method. The samples were fractionated, and characterized by osmotic pressure and light-scattering methods. Stress relaxation of the sample films was observed at various temperatures and the master curve was constructed by shifting the curves according to the time–temperature superposition principle. The steady-flow viscosity, the steady-state compliance, and other rheological parameters were calculated from the master curves. The molecular weight dependence and the branch density dependence of those rheological parameters were discussed based on the theories of Bueche and Graessley.

The effect of branching on viscoelastic properties of polymers has attracted a great interest of researchers because of the importance of the study in practical use of plastics. Beside the practical purpose, moreover, the study may be useful to understand the meaning of chain entanglement or the role of molecular conformation in the rheological behavior of polymers. In spite of many papers so far published,[1–9] however, no clear conclusion has been obtained concerning the effect of branching on the rheological properties. It has not even been definitely determined whether branching decreases the steady flow viscosity or not.[4,5,8,9] Reasons for lack of a clear conclusion may be various. First of all, experiments in which the samples were well characterized is scarce. Most samples used in previous works, with a few exceptions, were neither well purified nor well characterized. Considering the procedures of preparing the samples, they may have contained an amount of unbranched polymers. It is also certain that we need more systematic studies covering wide ranges of branch length and branch number.

There are various kinds of branched molecules: (1) star shaped, (2) comb shaped, and (3) randomly branched molecules. Most works have been done by using either star-shaped molecules or randomly branched molecules. In the present work, however, we report stress-relaxation data of a series of comb-shaped polystyrenes because it is possible to change both the degree of branching and the molecular weight of branch. Although the type of branching of the present samples is a comb type, however, these samples may more closely resemble star-shaped polymers than comb, because of the number and length of the branches relative to the backbone. There are not significant differences between the g_s values (defined later) calculated as star and those calculated as comb.

Samples. Reagents. The styrene monomer used was the first grade from the Katayama Chem. Co. It was fractionally distilled and dried with lithium aluminum hydride. It was then distilled *in vacuo* with benzophenone sodium and finally dried by passing through a tube of sodium mirror. Tetrahydrofuran used was the first grade from the Katayama Chem. Co. It was dried by distillation *in vacuo* in the presence of anthracene sodium.

The *n*-butyllithium was prepared by the method reported previously[10] and cumylpotassium was prepared by the method of Ziegler and Schnell.[11] Chloromethyl ether and other reagents were for laboratory use of Nakarai Chemicals, Ltd., and Katayama Chem. Co.

Preparation of Samples. The method of preparing comb-shaped polystyrenes was reported by Altares, *et al.*,[12] and also by the present authors.[13] The parent polymer was prepared by polymerization of styrene monomer with *n*-butyllithium in THF by the method of Szwarc.[14] The product was fractionated stepwise

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