

Physical Studies of Ionically-Terminated Polytetrahydrofuran Polymers. I. Dilute Solution Behavior

S. A. M. ALI* and D. J. HOURSTON†

The Polymer Centre, University of Lancaster, Lancaster, Lancashire, LA1 4YA, United Kingdom

SYNOPSIS

A series of tetrahydrofuran polymers, terminating at one end with a pyridinium bromide group, were prepared; their hydrodynamic behavior contrasted with the equivalent methoxy-terminated polytetrahydrofurans. This article reports viscometry studies of these polytetrahydrofurans in cyclohexane, toluene, tetrahydrofuran, methyl ethyl ketone, and cyclohexanone.

INTRODUCTION

The field of ion-containing polymers has experienced very rapid growth, both industrially and academically. The high level of activity is reflected in the appearance of books,^{1,2} as well as in a number of symposia. The main reason for this interest is undoubtedly the enormous range of potential applications for these materials. These applications, in turn, are due to the dramatic changes in the properties that result from the introduction of strong intra- and intermolecular Coulombic interactions, resulting from the presence of ions.

In this article, pyridinium bromide-terminated polytetrahydrofuran polymers (PTHF-Py) are compared with equivalent methoxy-terminated polytetrahydrofuran polymers (PTHF-OMe) to determine the effects of terminal ionic groups on the chain conformation in solution.

The concentration dependence of viscosity of dilute polymer solutions is commonly expressed³ as a power series in concentration (C).

$$\eta - \eta_s/\eta_s C = \eta_{sp}/C \\ = [\eta] + k_1[\eta]^2 C + k_2[\eta]^3 C^2 + \dots \quad (1)$$

Here η and η_s are the solution and the solvent viscosities, respectively, and η_{sp} is the specific viscosity.

$[\eta]$ is the intrinsic viscosity and k_1 and k_2 are dimensionless parameters.

Four common methods of obtaining $[\eta]$ by extrapolation were compared in an attempt to achieve the best values for further hydrodynamic investigations of these ionically-terminated polytetrahydrofuran polymers. The procedures selected were those developed by Huggins,⁴ Kraemer,⁵ Martin,⁶ and Schulz-Blaschke.⁷ The appropriate relations are shown in equations 2–5, respectively.

$$\eta_{sp}/C = [\eta] \{1 + k_H[\eta]C\} \quad (2)$$

$$\ln \eta_r/C = [\eta] \{1 - k_K[\eta]C\} \quad (3)$$

Here, η_r is the relative viscosity.

$$\ln (\eta_{sp}/C) = \ln [\eta] + k_M[\eta]C \quad (4)$$

$$\eta_{sp}/C = [\eta] \{1 + k_{SB}\eta_{sp}\} \quad (5)$$

Conventional extrapolations based on these four equations give only approximate values of $[\eta]$, some of which are overestimated, while others are underestimated. Averaging procedures, which give more correct values of $[\eta]$ of both good and poor solvents, have been suggested by Sakai.^{8,9} Also in this study, values of intrinsic viscosity for methoxy-terminated and pyridinium bromide-terminated polytetrahydrofuran polymers, of virtually the same molecular weight, are compared.

The values of Huggins constant, k_H , and $[\eta]$ for

* Present address: Institute of Medical and Dental Bioengineering, University of Liverpool, United Kingdom.

† To whom correspondence should be addressed.

these polymers were used to test the applicability of the Erich and Riseman¹⁰ relation shown below.

$$k_H[\eta]^2 = \alpha_E + \sigma_E[\eta] \quad (6)$$

α_E and σ_E are parameters, which depend on the particular system under investigation.

In addition, the semi-empirical relation proposed by Chou and Zakin^{11,12} was used to investigate correlations between the Huggins constants and the limiting viscosity numbers in various solvents.

EXPERIMENTAL

The polytetrahydrofuran polymers used in this work were synthesized by anionic polymerization, using a procedure which is already detailed¹³ in the literature. The PTHF-OMe and PTHF-Py series cover a relatively wide range of molecular weight. See Table I for characterization data.

All solvents used in this study were distilled and dried overnight over molecular sieve, prior to redistillation ($\times 2$), from which mid-cuts only were taken.

Measurement of Viscosity

The intrinsic viscosities of the samples were determined using Ubbelohde suspended-level viscometers

Table I Characterization Data and Sample Coding

Series	Code	\bar{M}_n^c	\bar{M}_w	\bar{M}_w/\bar{M}_n
PTHF-OMe ^a	R	4600	5428	1.18
	I	5600	6496	1.16
	A	10800	11556	1.07
	3	12000	12360	1.03
	5	16000	28640	1.79
	7	22000	38500	1.75
	J	24000	32400	1.35
	C	29000	36830	1.27
PTHF-Py ^b	G	44000	68640	1.56
	S	4700	5428	1.18
	B	10900	11556	1.07
	K	24100	32400	1.35
	D	29100	36830	1.27
	H	44100	68640	1.56

^a Methoxy-terminated polytetrahydrofuran.

^b Pyridinium bromide-terminated polytetrahydrofuran.

^c \bar{M}_n values were measured by vapor pressure osmometry (low \bar{M}_n) and membrane osmometry (high \bar{M}_n) and \bar{M}_w/\bar{M}_n was determined by GPC. \bar{M}_w was then calculated.

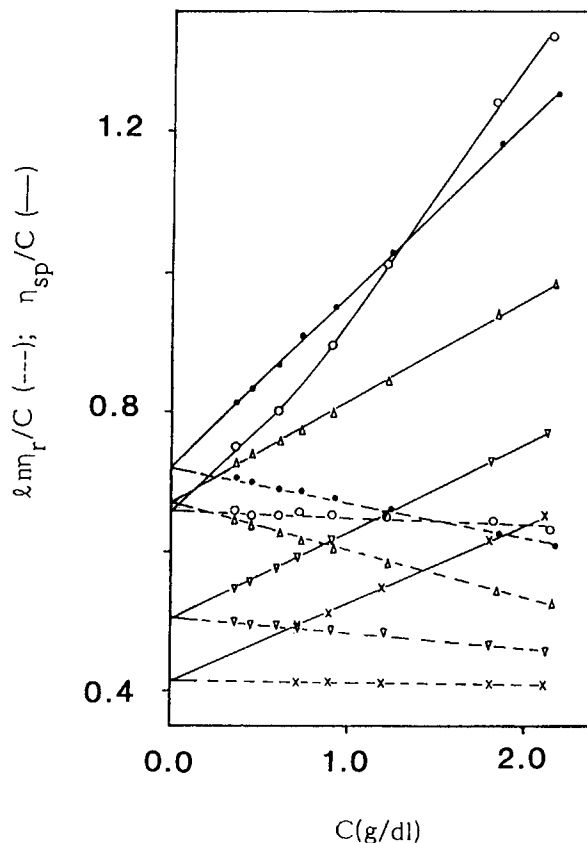


Figure 1 Huggins and Kraemer plots for sample H in cyclohexane (○), toluene (●), tetrahydrofuran (△), methyl ethyl ketone (×), and cyclohexanone (▽).

at $25^\circ \pm 0.01^\circ\text{C}$. Viscometers with solvent flow times of about 120–360 s were used. Filtered nitrogen, under pressure, was used to raise the liquid level in the viscometers. Three consecutive flow times, which agreed within at least ± 0.2 s, were recorded for each solution and then the average flow time was used. Shear corrections were not made because the limiting viscosity numbers were less than 3.00 dL/g.¹⁴ As the flow volumes of the viscometers used were greater than 5.00 mL, drainage errors¹⁵ for small capillaries were unimportant.

RESULTS AND DISCUSSION

Intrinsic Viscosities

Values of $[\eta]$ were obtained for the polymers in all of the five solvents (cyclohexane, toluene, tetrahydrofuran, methyl ethyl ketone, and cyclohexanone) using the four extrapolation procedures. It was observed that the limiting viscosity numbers, evaluated

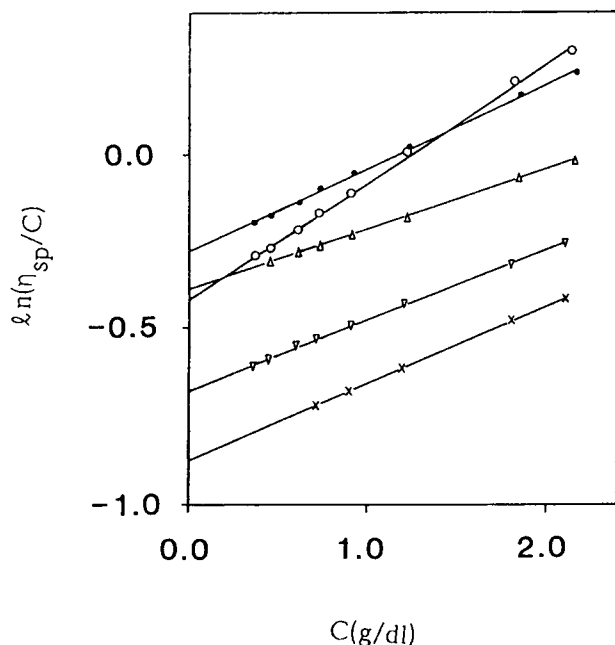


Figure 2 Martin plots for sample *H* in cyclohexane (○), toluene (●), tetrahydrofuran (△), methyl ethyl ketone (×), and cyclohexanone (▽).

by these four semi-empirical equations, were virtually identical for each polymer sample in any given solvent.

Linear plots were obtained with the Huggins relation (eq. 2) in all the systems studied except for the sample *H* PTHF-Py material in cyclohexane (see Figure 1). The concentration range studied was between 0.1% and 2.2% (w/v). The upward curvature, for this the highest molecular weight sample,

Table II Slope Constants Treated According to Sakai^{8,9} for Cyclohexane as Solvent

Series	Code	k_{H+K}	$\overline{k_{HM}}$	$\overline{k_{HSB}}$
PTHF-OMe	<i>R</i>	0.59	0.22	0.19
	1	0.80	0.83	0.71
	<i>A</i>	0.35	0.39	0.37
	3	0.69	0.57	0.56
	5	0.51	0.36	0.35
	7	0.52	0.39	0.37
	<i>J</i>	0.57	0.38	0.39
	<i>C</i>	0.63	0.50	0.50
	<i>G</i>	0.64	0.54	0.49
	<i>S</i>	0.63	0.18	0.15
PTHF-Py	<i>B</i>	0.56	0.48	0.52
	<i>K</i>	0.71	0.57	0.57
	<i>D</i>	0.57	0.46	0.49
	<i>H</i>	0.56	0.53	0.48

Table III Slope Constants Treated According to Sakai^{8,9} for Toluene as Solvent

Series	Code	k_{H+K}	$\overline{k_{HM}}$	$\overline{k_{HSB}}$
PTHF-OMe	<i>R</i>	0.43	0.12	0.12
	1	0.57	0.50	0.47
	<i>A</i>	0.54	0.38	0.36
	3	0.54	0.41	0.37
	5	0.47	0.31	0.29
	7	0.50	0.31	0.29
	<i>J</i>	0.56	0.36	0.35
	<i>C</i>	0.54	0.36	0.36
	<i>G</i>	0.53	0.36	0.33
	<i>S</i>	0.72	0.64	0.59
PTHF-Py	<i>B</i>	0.63	0.50	0.53
	<i>K</i>	0.61	0.44	0.43
	<i>D</i>	0.63	0.47	0.49
	<i>H</i>	0.59	0.40	0.41

could be caused by the neglect of the higher terms in eq. (1). Such upward curvature has, however, also been reported by Krause¹⁶ for micelles of block copolymers of styrene and methyl methacrylate in acetone and triethylbenzene, and also for styrene-butadiene block copolymers in methyl ethyl ketone and ethyl acetate, by Enyiegbulam.¹⁷

Linear plots were also obtained (Figure 1 is representative) when the Kraemer relation (eq. 3) was used. Huggins and Kraemer plots gave common intercepts in all cases.

With the Martin relation, the upward curvature observed for sample *H* in cyclohexane in the Huggins plot disappeared, as shown in Figure 2. This is a good illustration of the use of the Martin equation to compensate⁶ for curvature in Huggins plots, and indicates that the former explanation offered is more probable. Linear plots were also obtained in most

Table IV Slope Constants Treated According to Sakai^{8,9} for Tetrahydrofuran as Solvent

Series	Code	k_{H+K}	$\overline{k_{HM}}$	$\overline{k_{HSB}}$
PTHF-OMe	<i>R</i>	0.59	0.21	0.23
	<i>A</i>	0.43	0.17	0.16
	<i>J</i>	0.50	0.29	0.26
	<i>C</i>	0.48	0.31	0.30
	<i>G</i>	0.55	0.37	0.35
PTHF-Py	<i>S</i>	0.59	0.23	0.23
	<i>B</i>	0.31	0.10	0.10
	<i>K</i>	0.42	0.25	0.23
	<i>D</i>	0.47	0.28	0.28
	<i>H</i>	0.47	0.29	0.26

Table V Slope Constants Treated According to Sakai^{8,9} for Methyl Ethyl Ketone as Solvent

Series	Code	k_{H+K}	k_{HM}	k_{HSB}
PTHF-OMe	<i>R</i>	0.50	0.53	0.49
	1	0.48	0.42	0.39
	<i>A</i>	0.53	0.58	0.69
	3	0.67	0.55	0.58
	5	0.65	0.51	0.49
	7	0.52	0.41	0.35
	<i>J</i>	0.60	0.52	0.44
	<i>C</i>	0.75	0.65	0.63
	<i>G</i>	0.73	0.61	0.61
	PTHF-Py	<i>S</i>	0.48	0.49
<i>B</i>		0.59	0.59	0.57
<i>K</i>		0.71	0.63	0.64
<i>D</i>		0.70	0.65	0.66
<i>H</i>		0.62	0.57	0.58

systems with the Schulz-Blaschke equation. Downward curvature was, however, observed in a few cases, especially where the concentration exceeded 1.1% (w/v). Sakai^{8,9} has argued that the reason for such behavior, which was observed in this study for polymers with both types of end group, is that the Schulz-Blaschke equation predicts too rapid a rise of viscosity with concentration.

Slope constants

The following trends were observed in the slope constants obtained from eqs. (2)–(5).

$$k_H > k_M, \quad k_H > k_{SB} \quad \text{and} \quad k_M \geq k_{SB}$$

Table VI Slope Constants Treated According to Sakai^{8,9} for Cyclohexanone as Solvent

Series	Code	k_{H+K}	k_{HM}	k_{HSB}
PTHF-OMe	<i>R</i>	0.44	0.08	0.08
	1	0.66	0.70	0.58
	<i>A</i>	0.53	0.31	0.44
	3	0.50	0.34	0.39
	5	0.48	0.54	0.32
	7	0.49	0.26	0.25
	<i>J</i>	0.54	0.43	0.44
	<i>C</i>	0.54	0.42	0.43
	<i>G</i>	0.61	0.44	0.43
	PTHF-Py	<i>S</i>	0.35	0.00
<i>B</i>		0.59	0.38	0.38
<i>K</i>		0.61	0.42	0.41
<i>D</i>		0.54	0.42	0.42
<i>H</i>		0.60	0.46	0.39

Table VII k_{HM} , k_{HSB} Values in All the Solvents

Series	Solvent	k_{HM}	k_{HSB}
PTHF-OMe	Cyclohexane	0.46	0.44
	Toluene	0.35	0.33
	Tetrahydrofuran	0.27	0.26
	Methyl ethyl ketone	0.53	0.52
	Cyclohexanone	0.39	0.37
PTHF-Py	Cyclohexane	0.44	0.44
	Toluene	0.49	0.49
	Tetrahydrofuran	0.23	0.22
	Methyl ethyl ketone	0.59	0.58
	Cyclohexanone	0.34	0.32

These observations hold for both the methoxy- and the pyridinium bromide-terminated polytetrahydrofuran samples in all of the solvents. The observation that k_H is greater than k_{SB} has been reported for various homopolymer systems.¹⁸⁻²⁰

The highest k_H and the lowest $[\eta]$ values were obtained in methyl ethyl ketone, indicating that the solvent-polymer interactions are lower in this solvent than in the others. It has been reported²¹ that this solvent is a poor one for polytetrahydrofuran. The k_H values were 0.76 for the PTHF-OMe and 0.73 for the PTHF-Py polymers.

To find reasonable k_H values, Sakai^{8,9} suggested averaging procedures for both good and poor solvents. This clearly approximate procedure, which does not fully account for variations in the strengths of specific interactions even within the two solvent types, has been assessed using this data. The average values (k_{HM}) of k_H and k_M (good solvents) for the polytetrahydrofuran polymers in cyclohexane, toluene, tetrahydrofuran, methyl ethyl ketone, and cyclohexanone are shown in Tables II-VI. The averages (k_{HSB}) of k_H and k_{SB} (poor solvents) are also shown. The average values of k_{HM} and k_{HSB} in each solvent are shown in Table VII. These values may be used to ascertain whether the solvent is good or poor. Sakai^{8,9} has commented that k_H is 0.52 for an undrained coil under θ -conditions, and that 0.32 is typical for flexible chain polymers in good solvents. Consequently, methyl ethyl ketone is close to a θ -solvent, while tetrahydrofuran is a good solvent. It was noted (Table VII) that the average values of k_{HM} and k_{HSB} are very similar for each solvent. There was no evidence for any clear dependence of k_H on molecular weight for either the PTHF-OMe or the PTHF-Py materials. In the literature²² k_H has been reported to increase, to decrease, and to be independent of molecular weight.

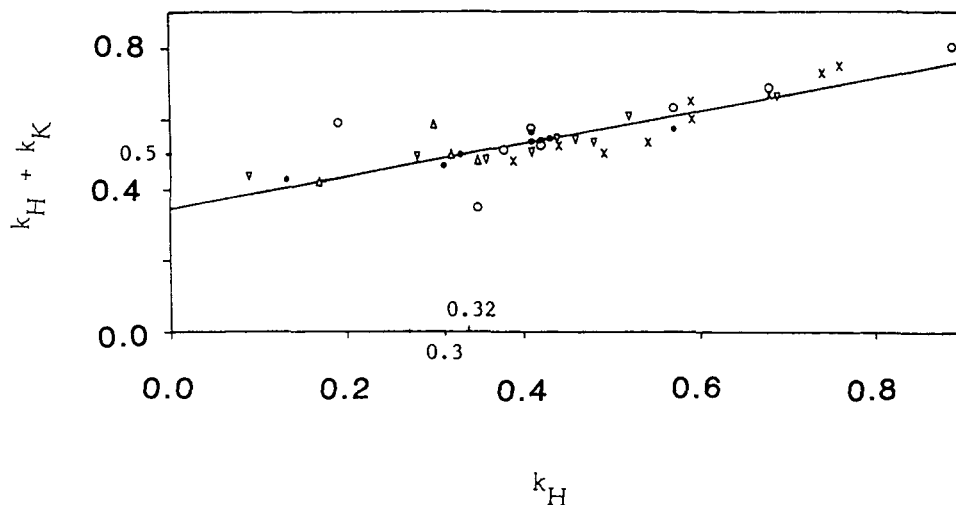


Figure 3 Plot of $k_H + k_K$ vs. k_H for the PTHF-OMe samples in cyclohexane (○), toluene (●), tetrahydrofuran (△), methyl ethyl ketone (×), and cyclohexanone (▽).

Closer examination shows that an approximately linear relationship exists between k_H and $k_H + k_K$ when the data for all solvents are so empirically plotted (see Fig. 3). The value of Huggins constant can be obtained when the assumption²² is made that $k_H + k_K$ is equal to 0.50. It was found by extrapolation that the k_H value for the methoxy-terminated polytetrahydrofuran (Fig. 3) was 0.33, and that the pyridinium bromide-terminated polytetrahydrofuran was 0.31. These two values are close to the predicted^{8,9} value of 0.32.

Another procedure used to redetermine k_H is to

plot k_{H+K} vs. k_H for each polymer sample in each of the five solvents. Figure 4 is a representative plot. The values of k_H redetermined by this method are given in Table VIII for each sample. The average value of the redetermined k_H for the methoxy-terminated polytetrahydrofuran polymers is 0.36 ± 0.07 , and the average value of the redetermined k_H for pyridinium bromide-terminated polytetrahydrofuran polymers is 0.34 ± 0.07 . These two values are again very similar to those predicted.^{8,9}

Therefore, plots of k_{H+K} vs. k_H , either for both series of polytetrahydrofuran polymers in a given

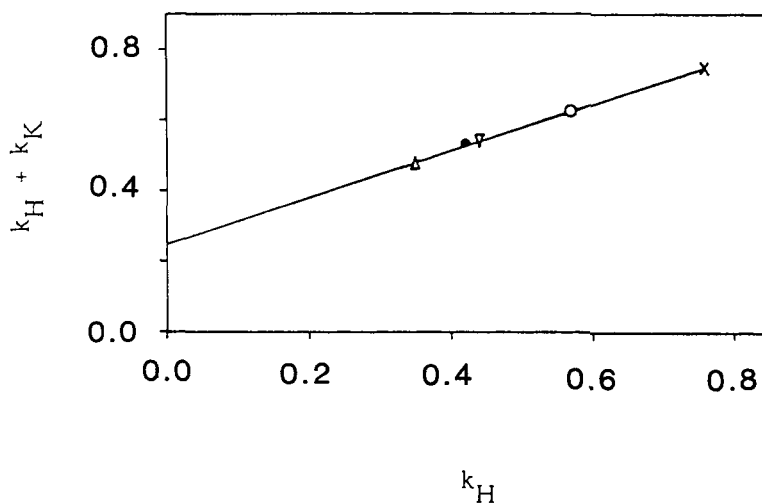


Figure 4 Plot of $k_H + k_K$ vs. k_H for sample C in cyclohexane (○), toluene (●), tetrahydrofuran (△), methyl ethyl ketone (×), and cyclohexanone (▽).

Table VIII Redetermined Values of k_H for Both Series of Polytetrahydrofuran Polymers in Several Solvents

Series	Code	k_H
PTHF-OMe	R	0.21
	1	0.44
	A	0.47
	3	0.38
	5	0.37
	7	0.35
	J	0.28
	C	0.38
PTHF-Py	G	0.34
	S	0.20
	B	0.40
	K	0.36
	D	0.37
	H	0.35

solvent or for a given polymer in a series of solvents, yield k_H values which are close to the ideal value of 0.32 predicted by Sakai.^{8,9}

Solvent's Effects on the Conformation of Polytetrahydrofuran

The quality and nature of the solvent affect the conformation of a polymer molecule in solution. To study further the effect of solvent type, the Eirich-Riseman¹⁰ equation was employed.

$$k_H[\eta]^2 = \alpha_E + \sigma_E[\eta] \quad (7)$$

α_E and σ_E are parameters that depend on the particular system under study. A plot was made of $k_H[\eta]^2$ vs. $[\eta]$ for each of the polymers in cyclohexane, toluene, tetrahydrofuran, methyl ethyl ketone, and cyclohexanone. A representative plot is shown in Figure 5. In most of the plots in both series, toluene occupied the highest position on each line while methyl ethyl ketone was at the bottom. This again illustrates that methyl ethyl ketone is a poor solvent for these polytetrahydrofuran polymers. It was also noticed that cyclohexane occupied a position near the bottom of each line in the methoxy-terminated polytetrahydrofuran series, but for the pyridinium bromide-terminated polytetrahydrofuran series, cyclohexane was near the top. This finding is attributed to the association of the ion-containing chains of the pyridinium bromide-terminated polytetrahydrofurans in this low dielectric constant solvent.

Dissociation, on dilution, was looked for, but not observed, in the concentration regime used.

Different methods have been proposed to correlate dilute solution viscosity data for linear flexible polymers^{12,23-26} by the construction of a single curve using the reduced dimensionless term, $C[\eta]$, in relation with the slope constants k_H or k_M . Chou and Zakin^{11,12} have used the Huggins slope constant, and have obtained a single curve using the following equation, which they thought to be a relation that should be applicable to polymers of molecular weight greater than 15,000, and up to $k_H[\eta]C$ values of 1.2, where C is the g/dL in good to fair solvents.

$$\frac{\eta_{sp}}{C[\eta]} = 1 + k_H[\eta]C \quad (8)$$

According to eq. (8), the data for the samples of the methoxy-terminated series and the pyridinium bromide-terminated series in cyclohexane, toluene, tetrahydrofuran, methyl ethyl ketone, and cyclohexanone have been plotted as shown in Figures 6 and 7, respectively. The slope and intercept were both found to be identical for the two series. The equation, therefore, holds for both series of polytetrahydrofuran polymers.

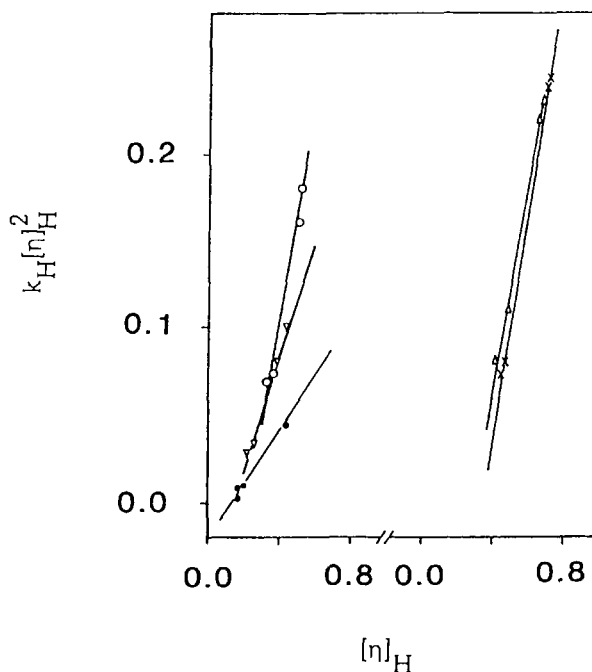


Figure 5 Plots of $k_H[\eta]^2$ vs. $[\eta]_H$ for the sample S (●), B (▽), K (○), D (×), and H (△) PTHF-Py polymers in the various solvents.

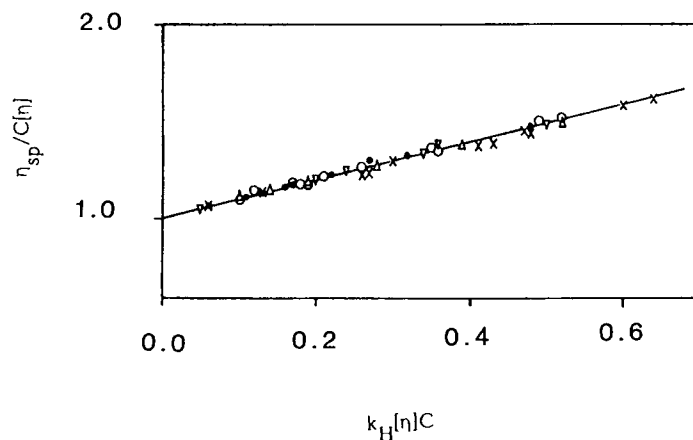


Figure 6 Plot of $\eta_{sp}/C[\eta]$ vs. $k_H[\eta]C$ for the PTHF-OMe samples in cyclohexane (○), toluene (●), tetrahydrofuran (Δ), methyl ethyl ketone (×), and cyclohexanone (∇).

Intrinsic Viscosities for Polytetrahydrofurans of Equal Molecular Weights

The only difference between samples *R* and *S*, or *C* and *D* (see Table I), is the replacement of nonionic methoxy ends of the polytetrahydrofuran chains with ionic pyridinium bromide groups. Thus, they differ only slightly in their molecular weights. Table IX shows the values of limiting viscosity numbers of these samples in the various solvents.

It was observed that the limiting viscosity numbers for samples *R*, *S*, and *C*, *D* in tetrahydrofuran, methyl ethyl ketone, and cyclohexanone are, within experimental error, the same. Thus, the introduction of ionic groups to the end of the polymeric chains

does not change the behavior of the coils in the dilute solutions of these solvents. In cyclohexane and toluene, the intrinsic viscosities of samples *S* and *D* were found to be higher than those of samples *R* and *C*. This is because of the low values of the dielectric constants of both cyclohexane (2.015 at 25°C) and toluene (2.379 at 25°C), which allows association to occur. In order to test this theory further, the viscosities of samples *G* and *H*, which are of high molecular weight, were studied in carbon tetrachloride, which also has a low value of dielectric constant (2.238 at 25°C). It was found that the limiting viscosity number of sample *H* was higher (0.94 compared with 0.41 dl/g) than sample *G* in this solvent.

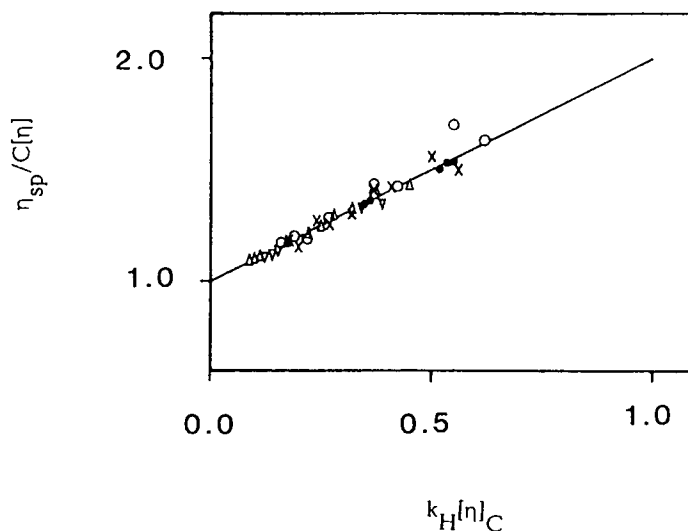


Figure 7 Plot of $\eta_{sp}/C[\eta]$ vs. $k_H[\eta]C$ for the PTHF-Py samples in cyclohexane (○), toluene (●), tetrahydrofuran (Δ), methyl ethyl ketone (×), and cyclohexanone (∇).

Table IX Molecular Weights and Intrinsic Viscosities of Samples R, S, C, and D

Solvent	[η] _H (dL/g)			
	Sample R (OMe)	Sample S (Py)	Sample C (OMe)	Sample D (Py)
Cyclohexane	0.16	0.22	0.42	0.71
Toluene	0.18	0.24	0.58	0.69
Tetrahydrofuran	0.18	0.18	0.61	0.62
Methyl ethyl ketone	0.14	0.14	0.38	0.37
Cyclohexanone	0.17	0.17	0.45	0.47
$\bar{M}_n \times 10^{-3}$	4.6	4.7	29.0	29.1

These observations illustrate the influence that the dielectric constant of the solvent can have on the dilute solution properties of these ion-containing polytetrahydrofurans.

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