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# Solubility and Properties of a Poly(aryl ether ketone) in Strong Acids

**Matthew T. Bishop, Frank E. Karasz,* and Paul S. Russo**[†]

*Materials Research Laboratory, Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003*

**Kenneth H. Langley**

*Department of Physics and Astronomy, University of Massachusetts, Amherst, Massachusetts 01003.* *Received January 11, 1984*

ABSTRACT: The properties of dilute solutions of poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (PEEK) in strong acids such as $H_2SO_4$ and $HSO_3Cl$ have been investigated by static and dynamic light scattering, absorption spectroscopy, and viscometry. Chemical modification of the original polymer has been found to occur when it is dissolved in some acids. This modification has implications with respect to both the process of dissolution itself and the solution properties observed.

## Introduction

Prior work on poly(aryl ether ketones) has focused on the synthesis,[1–4] thermal properties,[4] mechanical properties,[4] and crystal structure[5,6] of these polymers. To date, there have been no detailed reports on the dilute solution properties. In this work we have sought to determine the conformation in dilute solution, by combining the results of viscometry and static and dynamic light scattering, to gain some idea of the relative degree of flexibility or stiffness of these polymers and to see whether this information would in turn help to explain the reasons for the limited solubility of these polymers. Indeed, this limited solubility is a major obstacle to characterization of these polymers in solution.

Chosen for study as representative of this class of polymers was poly(ether ether ketone) (PEEK), with the repeat unit given in Figure 1a. This polymer is reported to be synthesized by a nucleophilic aromatic substitution reaction, using diphenyl sulfone as solvent, at temperatures approaching the melting point of the polymer.[4] As obtained, the material is highly crystalline. Prior experimental work to estimate relative molecular weights and to investigate structure, including branching, has utilized 98% $H_2SO_4$ as a solvent.[3,4] Syntheses of poly(aryl ether ketones) using poly(phosphoric acid)[3] and liquid HF[2] as solvents have also been reported. Room-temperature solubility of this polymer, as discussed more fully below, would thus appear limited to strong acids.[2–4]

With solvent choice thus circumscribed, we began our investigations using the strong acids $H_2SO_4$ and $HSO_3Cl$, initially neglecting the nature of these strong acids as reactants vis-à-vis the polymer. It soon became apparent that the polymer became sulfonated upon dissolution in $H_2SO_4$ and $HSO_3Cl$, as will be shown in detail below. Such sulfonation is to be expected.[7] Chemically similar polymers, for example poly(phenylene oxide)[8] and poly(aryl ether sulfones),[9] are readily sulfonated to yield ionic polymers with modified properties. Indeed, as reported in this paper, the dissolution of PEEK in various sulfonic acids, followed by recovery of the polymer, provides a route, albeit a rather poor one, to a new type of ionomer. Work to examine these new ionomers further is under way.

This chemical modification has been taken into account in explaining the results of the dilute solution studies. In particular, it has been related to varying degrees of "aggregation" observed in different solvents, in actuality chemical cross-linking due to side reactions of sulfonation. It has also been used to explain qualitatively the observed molecular weight and solvent dependence of the intrinsic viscosity, mutual diffusion coefficient (or the corresponding hydrodynamic radius), and the radius of gyration, as attributable to the expansion of the polyelectrolyte derivative of an inherently flexible polymer. By correcting for the degree of sulfonation, estimates of molecular weight (degree of polymerization) before dissolution have been obtained.

## Experimental Section

**Materials.** PEEK samples were generously provided by ICI Ltd., Welwyn Garden City, U.K. Samples (PEEK-1, -2, and -4) were dried at 110 °C under vacuum after rinsing with dust-free $H_2O$ and acetone. Concentrated $H_2SO_4$, assay 97.4%, (Fisher, ACS Reagent) was used without further purification. 100% $H_2SO_4$ was made by aqueous titration of dilute oleum after the procedure of Brand.[10] Chlorosulfonic acid (Aldrich), nominally 99%, was generally used without further purification, although in some early work the $HSO_3Cl$ was vacuum distilled. All other chemicals were reagent grade, used without further purification.

**Light Scattering. Sample Preparation.** All manipulations were performed in a dry $N_2$ atmosphere. Solutions were prepared by adding filtered solvent to known weights of polymer in volumetric flasks and then were clarified after complete dissolution by filtration directly into clean 10 × 75 mm Pyrex test tubes, which were then flame sealed. All filter assemblies used Teflon membrane filters (Millipore) of pore size 0.2 μm (97.4% $H_2SO_4$) or 0.5 μm (100% $H_2SO_4$, $HSO_3Cl$). For $HSO_3Cl$ solutions, the polyethylene backing, which is partially soluble in $HSO_3Cl$, had to be removed. Concentrations of PEEK in $H_2SO_4$, as measured by absorbance at 408 nm, were unaffected by filtration, even for the highest molecular weight sample. However, concentrations of PEEK in $HSO_3Cl$ were reduced by filtration.

**Dynamic Light Scattering.** These measurements were made on a spectrometer described elsewhere.[11] The light from the source, a Spectra-Physics Model 125 He–Ne laser, is vertically polarized, and all scattered light was detected. Correlation functions were thus $U_v$. No band-pass filter was used on the detection arm, since tests showed that fluorescence due to excitation at 632.8 nm had no noticeable effect on the observed correlation functions. Measurements were made at $\theta = 90°$ and $T = 30.0 \pm 0.1$ °C.

**Total Intensity Light Scattering.** These measurements were made by using a second spectrometer, which is capable of making both static and dynamic light scattering measurements. This apparatus has been described in detail elsewhere.[12] The incident light, the 514.5-nm line of a Spectra-Physics Model 165 Ar laser, is vertically polarized, and all scattered light was detected. The measured intensities were thus $U_v$. The incident beam was attenuated as required to prevent problems associated with thermal convection due to absorbance. A band-pass filter was used on the detector arm to remove fluorescent intensity. The photon-counting signal from the phototube, after suitable processing, was input into a Langley-Ford Instruments DC-64 correlator interfaced

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[†] Present address: Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803.

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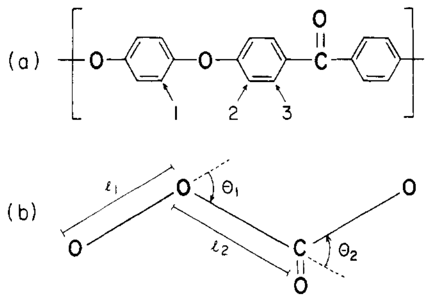

**Figure 1.** (a) Structure of poly(ether ether ketone) (PEEK). Positions marked with arrows are possible sites of substitution, either $SO_3H$ ($H_2SO_4$) or $SO_2Cl$ ($HSO_3Cl$). (b) Representation of PEEK as a chain of virtual bonds.

to a Tektronix 4051 microcomputer. Uncorrected intensities were obtained as either the count rate from the detector or as this same count rate divided by the count rate from a monitoring arrangement on the incident beam, this latter arrangement designed to remove the effects of laser intensity drift. In the former case, drift was monitored by frequent measurement of scattering from the secondary standard toluene. Rayleigh ratios were obtained by multiplying uncorrected excess intensities $I_{U_v}(\theta)$ by the correction factor $C = R_{U_v}(90°)/I_{U_v}(90°)$, where $R_{U_v}(90°) = 32.9 \times 10^{-6}$ cm$^{-1}$ is the Rayleigh ratio for toluene[13] and $I_{U_v}(90°)$ is the uncorrected intensity measured for toluene. Scattering angle range was 30–135°, and $T = 30.0 \pm 0.1$ °C. For each data point, at least 10 measurements of 2-s duration each were taken, thereby allowing estimation of statistical uncertainty in measured intensities and the removal of occasional spurious data. Refractive index increments (Figure 5) were measured with a previously calibrated differential refractometer, using different band-pass filters for measurements at different wavelengths. The accuracy of the total intensity spectrometer has been confirmed by measurements of samples of polystyrene and poly($\gamma$-benzyl glutamate) of known molecular weights.

**Viscometry.** Viscosities were measured with suspended-level Ubbelohde viscometers immersed in an oil bath maintained at 30.0 ± 0.1 °C under a dry $N_2$ atmosphere. Solvent efflux times were >100 s, to minimize kinetic energy effects.

**Absorption Spectra.** Absorption spectra were obtained on a Beckman Acta MIV spectrophotometer.

**NMR Spectra.** $^{13}C$ spectra were obtained on a Varian CFT-20 NMR spectrometer, $^{13}C$ irradiation frequency of 20 MHz, with broad-band $^1H$ decoupling.

**Recovery of PEEK after Dissolution in Acid.** Different procedures were required for $H_2SO_4$ and $HSO_3Cl$. Solutions of PEEK in $HSO_3Cl$ were added cautiously dropwise to excess $H_2O$ at 0 °C to precipitate the polymer. PEEK dissolved in $H_2SO_4$ was precipitated by addition of $H_2O$ at 0 °C. Precipitated polymers were shredded in a blender, washed very thoroughly with $H_2O$, and dried under vacuum at 25 °C over $P_2O_5$.

**Elemental Analysis.** Samples dried as above for at least 3 days were sealed in tubes under vacuum. All samples were tested for C/H/S; those precipitated from $HSO_3Cl$ were also tested for Cl.

**Titrations.** Samples were dissolved in DMF and titrated to a faint blue end point (thymol blue) with aqueous NaOH.

## Data Analysis

Intrinsic viscosities were obtained by the usual double extrapolation of reduced specific viscosity ($\eta_{sp}/c$) and inherent viscosity ($\ln \eta_r/c$) to infinite dilution. Concentrations had to be corrected for the degree of sulfonation in order to obtain correct results. Furthermore, measurements had to be made after the limiting degree of sulfonation was reached. All extrapolations were linear, with no evidence of the "anomalous" behavior which is typical of flexible polyelectrolytes at low concentration and low ionic strength.

Dynamic light scattering data were analyzed by the cumulants method,[14] with the quality of the data warranting expansion only to the quadratic (i.e., second cumulant) term. The measured second-order electric field correlation function $G^{(2)}(\tau)$, after base line subtraction and normalization, was fitted to the quadratic form

$$\ln \frac{G^{(2)}(\tau) - G^{(2)}(\infty)}{G^{(2)}(\Delta\tau) - G^{(2)}(\infty)} = C_0 - 2\langle\Gamma\rangle\tau + \mu_2\tau^2$$

where $\langle\Gamma\rangle$ and $\mu_2$ are the first and second cumulants, respectively. The first cumulant $\langle\Gamma\rangle$ is an average decay rate, which can be related to $D_z$, the $z$-average translational diffusion coefficient:

$$D_z = \langle\Gamma\rangle/q^2$$

where $q = (4\pi n/\lambda_0) \sin(\theta/2)$. The second cumulant $\mu_2$, which is the second moment of the decay rate distribution, after suitable normalization (i.e., $\mu_2/\langle\Gamma\rangle^2$) provides a rough measure of the polydispersity.

In fitting the data, both calculated and measured base lines $G^{(2)}(\infty)$ were used, with no significant difference between the two for samples in $H_2SO_4$. In each case, calculated $G^{(2)}(\infty)$ was determined as the square of the (measured) average intensity, and measured $G^{(2)}(\infty)$ was determined from the last eight channels (delayed by 64 $\Delta\tau$) of the correlation function. Values of $D_z$ for the same sample at different concentrations were linearly extrapolated to $c = 0$ to approximately eliminate intermolecular interaction effects. Ideally, one also should extrapolate to sample time $\Delta\tau = 0$; however, this correction was neglected. Effective hydrodynamic radii $\langle R_H\rangle_z$ (subsequently referred to as $R_H$) were then calculated:

$$\langle R_H\rangle_z = \frac{k_B T}{6\pi\eta_s D_{z,0}}$$

In parts a–c of Figure 2 are shown a typical experimental correlation function, the cumulant fit to that data, and the error in the fit.

Total intensity light scattering data were analyzed by the method of Zimm.[15] $Kc_u/R_{U_v}(\theta)$ was plotted as a function of $\sin^2(\theta/2) + kc_u$, where the optical constant $K = 4\pi^2 n^2 (dn/dc)^2/\lambda_0^4 N_A$ and $R_{U_v}(\theta)$ is the $U_v$ Rayleigh ratio at scattering angle $\theta$. Depolarized scattering was assumed to be negligible (measured $\rho_V(90°) \lesssim 0.01$); hence no Cabannes factor correction was applied. It is important to note that the concentrations $c_u$ used in the initial analyses were concentrations *before sulfonation*. Therefore the apparent results (denoted by the subscript a) which were obtained, namely the weight-average molecular weight $(\bar{M}_w)_a$, the $z$-average radius of gyration $(\langle R_G^2\rangle_z^{1/2})_a$ (subsequently referred to as $R_G$), and the second virial coefficient $(A_2)_a$, had to be corrected for the effects of sulfonation. Actual concentrations of the sulfonated polymer were, of course, higher. To a good approximation

$$c_s = \beta c_u$$

where $\beta$ is the factor by which the polymer weight increases upon sulfonation. Subscript u denotes unsulfonated PEEK, and s denotes sulfonated PEEK. Thus the initial Zimm plots were actually $Kc_s/\beta R_{U_v}(\theta)$ vs. $\sin^2(\theta/2) + kc_s/\beta$. Thus $(\bar{M}_w)_s = \beta^{-1}(\bar{M}_w)_a$ and $(\bar{M}_w)_u = \beta^{-1}(\bar{M}_w)_s$, so that $(\bar{M}_w)_u = \beta^{-2}(\bar{M}_w)_a$. Also, $(R_G)_s = (R_G)_a$, and $(A_2)_s = (A_2)_a$. Both $(R_G)_u$ and $(A_2)_u$ are of course inaccessible in these experiments.

Solutions of PEEK in 97.4% $H_2SO_4$ are yellow. They absorb strongly and fluoresce. Since both absorbance and fluorescence affect measured intensities, they must be corrected for to obtain accurate results.[16] As mentioned in the Experimental Section, a band-pass filter at the incident (scattered) wavelength was employed. We have

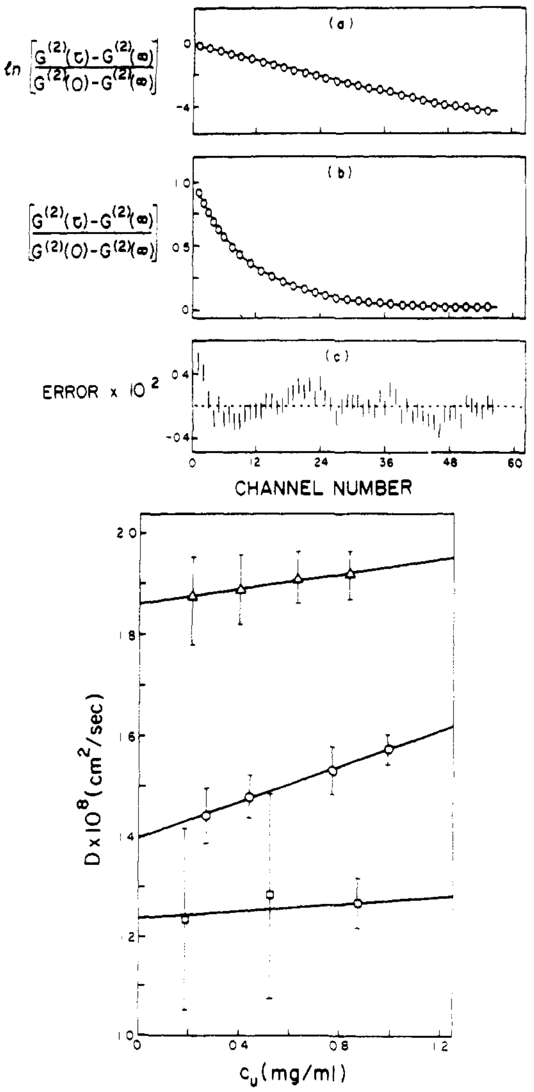

**Figure 2.** Typical dynamic light scattering results. Parts a–c are for PEEK-2/97.4% $H_2SO_4$, $c_u = 0.266$ mg/mL, $\theta = 90°$, $T =$ 30.0 °C, and $\Delta\tau = 1 \times 10^{-4}$ s, with the calculated base line. (a) Experimental ln $\{[G^{(2)}(\tau) - G^{(2)}(\infty)]/[G^{(2)}(0) - G^{(2)}(\infty)]\}$ and the second-order cumulant fit to the data. (b) Base line subtracted and normalized autocorrelation function (experimental and fitted). (c) Error in each channel for the fitted autocorrelation function. (d) Extrapolation of experimental values of $D_z$ in 97.4% $H_2SO_4$ to $c_u = 0$. ((△) PEEK-1; (○) PEEK-2; (□) PEEK-4).

assumed that this effectively filtered out the fluorescent intensity, which has a maximum at a wavelength significantly removed from the incident wavelength. The coefficients of absorption at a given wavelength ($\epsilon_\lambda$) which were required in order to correct measured intensities were obtained by measuring the absorbance $A_\lambda$ of solutions of known concentration $c_u$ in cells of known path length $l$; $\epsilon_\lambda = A_\lambda/c_u l$. Specifically, we obtained absorption coefficients from measurements of $A_{514.5\ \mathrm{nm}}$. Values obtained for $\epsilon_\lambda$ in $H_2SO_4$ at 514.5 nm were approximately 125 cm³ g-cm (or less), yielding a negligible correction in $(\mathrm{d}n/\mathrm{d}c)^2$. As will be discussed subsequently, the absorbance changes with time, due to increasing sulfonation of the polymer. Both light scattering and absorbance measurements were made after sufficient time was allowed for the limiting level of sulfonation to be reached. Absorbance corrections were imperative for the correct determination of $A_2$, somewhat less so for $R_G$, and, at least in 97.4% $H_2SO_4$, had little effect on $\bar{M}_w$ determination.

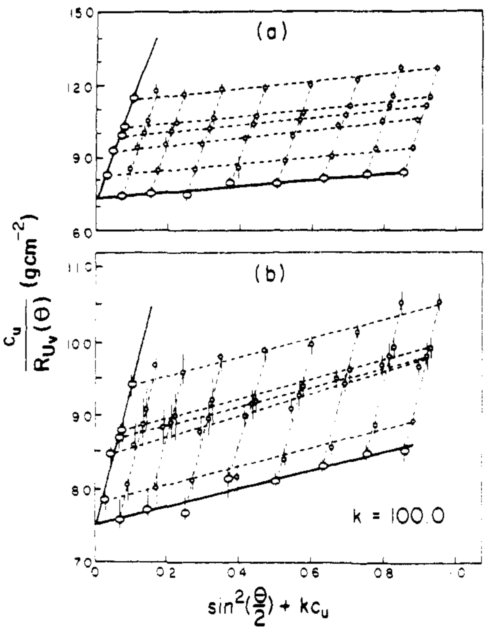

**Figure 3.** Typical Zimm plot for PEEK-2 in 97.4% $H_2SO_4$: (a) before absorbance correction; (b) after absorbance correction.

Shown in Figure 3 is a typical Zimm plot, illustrating the effect of the absorbance corrections. Error bars incorporate only the uncertainty in those scattered intensities (solution, solvent, and secondary standard toluene) which enter into the calculation of the excess Rayleigh ratio at each point. The standard deviation of intensity integrated over 2 s (obtained from 20 measurements of 2-s duration) was used to estimate the uncertainty in scattered intensities. This overestimates the error by a factor of about $20^{1/2}$; however, the enhanced size of the error bars aids in seeing the relative weights accorded the data. Use of these measured standard deviations as *relative* weights was deemed preferable to the use of Poisson estimates of error, because coherence time effects were evident at low angles for measurements of PEEK in these solvents on our apparatus. The ability to examine the fluctuation of measured intensities is a useful feature of a photon-counting total intensity light scattering spectrometer. Uncertainties in measuring concentrations, angles, and absorbance coefficients were ignored in making error estimates, because the relative uncertainty in those quantities was considerably less than the uncertainty due to fluctuations in measured intensities. The uncertainty in the Rayleigh ratio of toluene[13] was taken into account when estimating error in the various quantities derived from the Zimm plots (Table I).

## Results and Discussion

PEEK was characterized most completely in 97.4% $H_2SO_4$. Three unfractionated PEEK samples were used, designated as PEEK-1, -2, and -4, in order of increasing molecular weight. Figure 2d shows the extrapolation of $D_z$ values to infinite dilution. All other results, including estimates of molecular weights before dissolution, are given in Table I.

Intrinsic viscosity and light scattering results were combined to obtain a more complete picture of the behavior of PEEK when dissolved in 97.4% $H_2SO_4$. Obviously these results are directly related only to the substantially modified, sulfonated PEEK. Double-logarithmic plots of $[\eta]$, $R_G$, and $R_H$ vs. $(\bar{M}_w)_s$ are shown in Figure 4.

The initial picture one might draw from these results is that PEEK in 97.4% $H_2SO_4$ is an inherently flexible coil expanded by electrostatic, and possibly other thermodynamic, interactions. All the results are fairly consistent within the error limits of the measurements.

Table I
Properties of PEEK Dissolved in 97.4% $H_2SO_4$

| | PEEK-1 | PEEK-2 | PEEK-4 |
|---|---|---|---|
| $[\eta]$, dL $g^{-1}$ | 0.716 ± 0.002 | 0.931 ± 0.003 | 1.124 ± 0.005 |
| $(\bar{M}_w)_a$ | 31 800 ± 1000 | 52 000 ± 1500 | 57 100 ± 1700 |
| $(\bar{M}_w)_s{}^a$ | 24 900 ± 800 | 40 700 ± 1200 | 44 700 ± 1300 |
| $(\bar{M}_w)_u{}^a$ | 19 500 ± 600 | 31 900 ± 900 | 35 000 ± 1100 |
| $R_G$, Å | 155 ± 40 | 204 ± 26 | 212 ± 22 |
| $A_2$, mol $cm^3$ $g^{-2}$ | $(2.27 \pm 0.32) \times 10^{-3}$ | $(2.52 \pm 0.35) \times 10^{-3}$ | $(2.32 \pm 0.32) \times 10^{-3}$ |
| $R_H$, Å | 70.2 ± 3.4 | 93.7 ± 3.7 | 106 ± 18 |
| $R_H/R_G$ | 0.45 ± 0.12 | 0.46 ± 0.06 | 0.50 ± 0.10 |

[a] Calculated assuming $\beta = 1.28 \pm 0.01$, corresponding to one $SO_3H$ group per repeat unit, $X_E = 1.00 \pm 0.02$. Here $\beta = [288.3 + (X_E \times 80.06)]/288.3$.

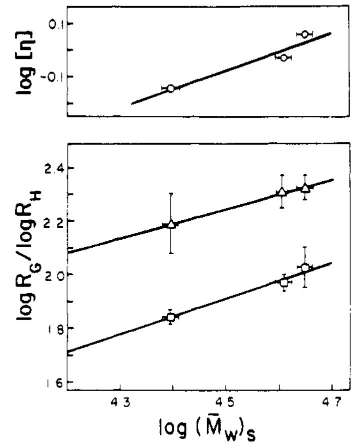

**Figure 4.** (a) Intrinsic viscosity $[\eta]$ as a function of molecular weight of sulfonated polymer $(\bar{M}_w)_s$. (b) Dependence of radius of gyration $R_G$ (△) and hydrodynamic radius $R_H$ (○) on $(\bar{M}_w)_s$. Lines shown were fitted to the data assuming power law relationships.

One might usually assume, as is implicit in the double-logarithmic plots, that the molecular weight dependence of equilibrium and nonequilibrium properties of PEEK dissolved in 97.4% $H_2SO_4$ can be adequately represented by power laws of the general form

$$a = KM^b$$

Whether this assumption is reasonable must be considered. For example, it is suggested that properties of polymers which can be better modeled as wormlike chains show a more complicated molecular weight dependence, which is perhaps better represented by equations of the form[17]

$$a = KM^b + K'$$

Certainly the quality, and quantity, of our data is such that we have little grounds for choosing one model over another. As a consequence, the conclusions which can be drawn are limited. (We note that the molecular weight range spanned by the samples available was fairly narrow.)

Treating PEEK as a wormlike chain, the persistence length $a$ was estimated by means of the equation relating that quantity to the mean square radius of gyration $\langle R_G{}^2 \rangle$ and the contour length $L$.

$$\langle R_G{}^2 \rangle = \frac{La}{3} - a^2 + \frac{2a^3}{L} - \frac{2a^4}{L^2}(1 - e^{-L/a})$$

Contour lengths were calculated as

$$L_z = n_z(l_1 + 2l_2) \cos (\theta/2)$$

attempting to approximately correct to $z$-average for comparison with $\langle R_G{}^2 \rangle_z$ from light scattering. Here, $n_z$ = $z$-average number of repeat units = $1.5(\bar{M}_w)_u/288.3$, with 288.3 the weight per repeat unit and with the factor 1.5 approximately correcting $(\bar{M}_w)_u$ to $(\bar{M}_z)_u$, assuming as is reasonable a most probable molecular weight distribution. Lengths $l_1 = 5.50$ Å and $l_2 = 5.62$ Å represent respectively the lengths of the oxy-1,4-phenyleneoxy and oxy-1,4-phenylenecarbonyl virtual bonds (Figure 1b). Here $\theta = \theta_1 = \theta_2$ is the bond angle supplement. Although the bond angle supplements $\theta_1$ and $\theta_2$ (Figure 1b) are both reported to be 54–55° in crystalline PEEK[5,6], it is questionable whether these angles would be the same in solution. For example, the bond angle supplement in poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is reported to be 56° in the crystalline polymer[18] but 61° in solution.[19-21] Although justified only by the PEEK crystal structure and by crude analogy to PPO, for the sake of these calculations we took $\theta_1 = \theta_2 = \theta$ with a range $55° < \theta < 61°$. The results were found to be fairly insensitive to bond angle over this range.

The following values for persistence length $a$ gave very good agreement between calculated and measured $\langle R_G{}^2 \rangle_z$ values. For $\theta = 55°$, $a = 53$ Å, giving $\langle R_G{}^2 \rangle_z{}^{1/2}$ = 155, 202, and 212 Å for PEEK-1, -2, and -4, respectively; for $\theta = 61°$, $a = 55$ Å, giving $\langle R_G{}^2 \rangle_z{}^{1/2}$ = 155, 203, and 213 Å. This value for the persistence length, $a \approx 54$ Å (or Kuhn length $\lambda^{-1} \approx 108$ Å) indicates that PEEK in 97.4% $H_2SO_4$ is somewhat "stiff". The parameter $L/a$ ranges from about 25 to 50 for the polymers studied.

Values for $L$ and $a$, together with reasonable estimates of other molecular hydrodynamic parameters, indicate that some draining is to be expected for these polymers. This is directly confirmed by the relatively low $R_H/R_G$ ratios observed. Furthermore, although sizable error certainly prevents a firm conclusion, there is some indication that as molecular weight and hence $L/a$ increase, the $R_H/R_G$ ratio increases, indicating decreased draining as would be expected.

Before discussing these results further, it is worthwhile to consider the nature of PEEK dissolved in $H_2SO_4$. The polymer is no longer neutral but bears ionic charges due to protonation. The $SO_3H$ groups resulting from sulfonation of the polymer are partially protonated in solution.[22] Carbonyls in the main chain are essentially 100% protonated,[23] and protonation of the phenyl rings of the polymer (i.e., electrophilic addition of $H^+$) would also be expected to occur to some extent.[23]

The unperturbed dimensions of this protonated, sulfonated PEEK would be expected to exceed those of neutral, unsulfonated PEEK. Arguments are presented below to the effect that PEEK dissolved in 97.4% $H_2SO_4$ is not greatly expanded by long-range interactions. Hence an estimate of the unperturbed dimensions of unmodified PEEK would allow estimation of the extent to which protonation and sulfonation give rise to short-range interactions which expand the chain.

The PEEK chain can be represented as a succession of two types of virtual bonds, as shown in Figure 1b. For polymers with structures similar to PEEK, for example, poly(2,6-disubstituted-1,4-phenylene oxides), and the po-

**Table II**
**Dynamic Light Scattering: PEEK in Various Acidic Solvents**

| | calcd base line | | measd base line | | solvent | | |
|---|---|---|---|---|---|---|---|
| polymer | $R_H$, Å | $\mu_2/\langle\Gamma\rangle^2$ | $R_H$, Å | $\mu_2/\langle\Gamma\rangle^2$ | initial | final | $c_u$, mg/mL |
| PEEK-2 | 108.8 | 0.195 | 108.9 | 0.164 | 100% $H_2SO_4$ | 100% $H_2SO_4$ | 0.466 |
| PEEK-2 | 119.4 | 0.237 | 111.9 | 0.185 | 100% $H_2SO_4$ | 95% $H_2SO_4$ | 0.419 |
| PEEK-2 | 105.5 | 0.205 | 104.5 | 0.168 | 100% $H_2SO_4$ | 90% $H_2SO_4$ | 0.364 |
| PEEK-2 | 88.4 | 0.158 | 88.5 | 0.155 | 97.4% $H_2SO_4$ | 97.4% $H_2SO_4$ | 0.439 |
| PEEK-4 | | | 102.3 | 0.206 | 97.4% $H_2SO_4$ | 97.4% $H_2SO_4$ | 0.514 |
| PEEK-4 | | | 126.4 | 0.272 | $HSO_3Cl$ | $HSO_3Cl$ | 0.467 |

lycarbonate of bisphenol A, both theoretical calculations of the conformational energies of rotational isomers[24] and experimental results on the unperturbed dimensions in solution[19-21] have shown that representation of these polymers as freely rotating chains of virtual bonds provides a reasonable description of their equilibrium properties in the unperturbed state. The extension of these arguments to PEEK follows from the observations that (1) the rotation angle about a given virtual bond is the sum of two statistically independent rotations about real bonds[24] and (2) the rotational potentials about the real bonds would by symmetric about rotation angles of 0, $\pi$, ... and $\pi/2$, $3\pi/2$, ...

The unperturbed dimensions of unmodified PEEK were thus estimated by using this model of a freely rotating chain of three virtual bonds per repeat unit.

$$\langle R_G^2\rangle_{z,0} = \frac{n_z}{6(1-\cos^3\theta)}\{(l_1^2 + 2l_2^2)(1+\cos^3\theta) + (4l_1l_2 + 2l_2^2)(\cos\theta + \cos^2\theta)\}$$

Here $n_z$, $l_1$, $l_2$, and $\theta$ are as discussed in calculation of the persistence length; that is, an attempt was made to correct to $z$-average dimensions, and bond angle supplements were taken to be equal and in the range 55–61°. These calculations indicate that the dimensions of PEEK in 97.4% $H_2SO_4$ are expanded by a factor of about 2.0–2.4 relative to the unperturbed dimensions of unmodified PEEK.

This expansion of protonated, sulfonated PEEK could be attributable to one or more of the following: short-range interferences to free rotation, thermodynamic interactions of PEEK with the solvent, and long-range repulsive electrostatic forces between charges on the chain.

We speculate that short–range hindrances to rotation might arise from the following: introduction of bulky $SO_3H$ groups; greater steric interactions of protonated phenyl rings, compared with unprotonated phenyl rings; short-range repulsive electrostatic forces between protonated sites on the chain; and increased tendency for coplanarity of phenyl rings with protonated carbonyls, in order to delocalize the charge.

Thermodynamic interaction of PEEK with the solvent cannot be simply estimated. However, we would not expect $H_2SO_4$ to be a "good" solvent for PEEK in the usual thermodynamic sense.

Long-range electrostatic forces would be predicted to have a relatively minor effect on the expansion of PEEK in 97.4% $H_2SO_4$. The Debye screening length $\kappa^{-1}$ is calculated to be about 2 Å in 97.4% $H_2SO_4$, for estimated concentration of ionic species of 2.4 M (1.3 $m$).[25] Although at this concentration the assumptions on which the calculation is based are of dubious validity, it is clear that long-range electrostatic forces should be extensively screened. Further evidence of screening is shown by the linear behavior of $\eta_{sp}/c$ and $\ln \eta_{rel}/c$ vs. $c$. It seems reasonable to conclude that the overall expansion is largely the result of relatively short-range steric and electrostatic interactions, and only to a lesser degree a manifestation of thermodynamic solvent quality and/or long-range polyelectrolyte expansion.

Application of two-parameter theory[17] to the results of light scattering ($A_2$, $\langle R_G^2\rangle_z$, and $(\bar{M}_w)_s$) also supports this conclusion. Calculations give the result that expansion relative to some hypothetical unperturbed state must be relatively slight ($\alpha_{R_G} < 1.05$) and furthermore that such modest expansion could account for the values of $A_2$ observed. Such application of the two-parameter theory is *perhaps* loosely justified in this case, resting on the assumption that classical (i.e., Donnan) contributions to apparent excluded volume would be negligible due to the quite high ionic strength.

This latter assumption is supported by calculations of ideal Donnan contributions[26] $A_2°$. For reasonable values of charge per repeat unit ($Z$ = 1, 2, and 3) one obtains values of $A_2° = 7.6 \times 10^{-4}$, $3.0 \times 10^{-3}$, and $7.0 \times 10^{-3}$ mol cm$^3$ g$^{-2}$. These are of the same order of magnitude as the experimental second virial coefficient. This should be compared with the usual result for typical polyelectrolytes, where the experimental $A_2$ values are usually found to be 1–2 orders of magnitude lower than the ideal Donnan terms $A_2°$, the difference attributable in large part to failure to use the true activities of polyions, counterions, and added salt in the calculation of $A_2°$. In this case one would by analogy expect the actual Donnan contribution to $A_2$ to be far lower than the ideal $A_2°$ values calculated above, and hence negligible. However, this conclusion could only be put on a firm basis with knowledge of the activities of various ions in 97.4% $H_2SO_4$, with and without dissolved polymer.

A tentative overall picture is that sulfonated and protonated PEEK is expanded by relatively short-range steric and electrostatic interactions to what is in essence a quasi-unperturbed state, with quasi referring to the inclusion of the short-range *electrostatic* interactions. Further slight expansion of this quasi-unperturbed state by those "long-range" electrostatic forces which are not completely screened is perhaps the major cause of nonideality, with some additional excluded volume contribution due to the Donnan effect. This expanded PEEK, at least for the molecular weights studied here, would appear best represented as a partially draining wormlike coil, perhaps with excluded volume.

Results of experiments in other strong acids further complicate the picture. Table II shows $R_H$ and $\mu_2/\langle\Gamma\rangle^2$ for PEEK samples in various acids, at comparable concentration. Especially noteworthy is the observation that the $R_H$ of the PEEK-2 which was initially dissolved in 100% $H_2SO_4$ is essentially constant regardless of the ultimate acid strength and is significantly different from the $R_H$ of PEEK-2 dissolved in 97.4% $H_2SO_4$. Similarly, $R_H$ of PEEK-4 in $HSO_3Cl$ is greater than in 97.4% $H_2SO_4$. In all cases, the polydispersity parameter $\mu_2/\langle\Gamma\rangle^2$ is seen to increase in the stronger acids; curvature in the $\ln |g^{(1)}(\tau)|$ plots is marked.

Analysis of total intensity light scattering measurements of PEEK-1 and PEEK-4 dissolved in $HSO_3Cl$, after ap-

Table III
Analysis of Recovered Polymers

| sample | solvent | time,[a] days | $c_u$, mg/mL | $X_E$ | acid value, mequiv/g | |
|---|---|---|---|---|---|---|
| | | | | | measd | calcd[b] |
| PEEK-2 | 97.4% $H_2SO_4$ | 3 | 9.9 | 0.63 | 2.13 | 1.86 |
| PEEK-2 | 97.4% $H_2SO_4$ | 33 | 8.6 | 1.00 | 2.78 | 2.71 |
| PEEK-2 | 100% $H_2SO_4$ | 3 | 10.8 | 0.98 | 2.70 | 2.67 |
| PEEK-3 | $HSO_3Cl$ | 0 | 10.0 | 0.90 | 5.04 | 4.78 |
| PEEK-3 | $HSO_3Cl$ | 7 | 10.0 | 1.50 | 6.76 | 6.87 |

[a] Elapsed time from complete dissolution until precipitation. [b] Using value of $X_E$ from elemental analysis.

proximate correction for the time-dependent absorbance changes, the concentration changes during filtration, and the degree of chlorosulfonation, gave values for $(\bar{M}_w)_u$ and $R_G$ significantly higher than the values found in 97.4% $H_2SO_4$. The severe plugging of 0.5-$\mu$m Teflon filters which was observed during clarification of PEEK-$HSO_3Cl$ solutions was never observed for PEEK in $H_2SO_4$, even for PEEK-4 in 100% $H_2SO_4$. Previous work in this laboratory,[27] using distilled $HSO_3Cl$ and 5-$\mu$m sintered glass for clarification, gave still higher values for $R_H$, $R_G$, $\bar{M}_w$, and $\mu_2/\langle\Gamma\rangle^2$. For PEEK-1 and PEEK-4, respectively, $(\bar{M}_w)_a$ = 114000/2020000, $R_G$ = 349/1300 Å, and $R_H$ = 412/1990 Å.

These results indicate either increased aggregation or expansion in the stronger acids. The former possibility, namely aggregation, could be attributed to physical aggregation after dissolution, to aggregation via chemical reaction, or to poorer solubility of PEEK in stronger acids. In fact, PEEK was seen to have *better* solubility in stronger acids. Also, physical aggregation appears unlikely, at least as the principal cause, as shown by the experiment where PEEK dissolved in 100% $H_2SO_4$ remained the same size even when acid strength was changed.

One might perhaps expect different degrees of expansion in the different acids due to variations in the Debye screening length $\kappa^{-1}$; however, upon closer examination it is obvious that variations in ionic strength cannot account for the magnitude of the observed effects. Calculations of $\kappa^{-1}$ for different strengths of $H_2SO_4$ indicate that even in 100% $H_2SO_4$ the concentration of ions due to the various ionization equilibria[25] should be sufficient to effectively suppress polyelectrolyte expansion due to charges separated by relatively large distances. This is also claimed to be the case in $HSO_3Cl$,[28] with ionic strength approximately $2 \times 10^{-3}$ M. Also, although expansion would affect measurements of $R_G$ and $R_H$, it should not affect $\bar{M}_w$ measurements as greatly as seen, unless depolarization by the extended chain and hence the Cabannes factor increased greatly. These arguments lead to the conclusion that "aggregation" due to chemical reaction is the major cause of the effects seen in the stronger acids 100% $H_2SO_4$ and $HSO_3Cl$.

The occurrence of cross-linking reactions in these acid media is indeed reasonable.[7,22,23] Cross-linking would be due to formation of sulfone links between aromatic rings on different polymer molecules. Intramolecular cross-links would also be possible. Sulfone formation concurrent with sulfonation and chlorosulfonation of polymers has been observed previously by various workers: for example, upon dissolving a heterocyclic semi-ladder polymer in fuming $H_2SO_4$[29] and when modifying polystyrene by reaction with $HSO_3Cl$.[30] The tendency toward sulfone formation increases in the order 97.4% $H_2SO_4$ < 100% $H_2SO_4$ ≪ $HSO_3Cl$, with this being the same order found for increasing "aggregation". Furthermore, the experiments performed in distilled $HSO_3Cl$,[27] where the formation of pyrosulfuryl chloride ($S_2O_5Cl_2$) is unavoidable,[31] showed still higher "aggregation", explainable by the even greater tendency for sulfone formation in the presence of $S_2O_5Cl_2$.[22]

An estimate of the extent of intermolecular sulfone formation $\rho_c$ beyond which infinite gel can occur is given by[32]

$$\rho_c = (\bar{Y}_w - 1)^{-1}$$

where $\bar{Y}_w$ is the weight-average number of units capable of participating in cross-linking. PEEK is sulfonated to the extent of approximately one group per repeat unit; hence $\bar{Y}_w$ is essentially the weight-average degree of polymerization. Thus $\rho_c$ ranges from 0.015 for PEEK-1 to 0.008 for PEEK-4. Even below these levels, cross-linking to noninfinite size would still occur. As a typical example, sulfonation of benzene by $HSO_3Cl$ yields diphenyl sulfone to the extent of 5–20%.[22] Even given that intramolecular sulfone formation would probably exceed intermolecular, with the ratio dependent on concentration, one can see why serious problems associated with cross-linking were encountered in studying PEEK in $HSO_3Cl$ (e.g., filter plugging, microgels). In contrast, sulfone formation in aqueous $H_2SO_4$, for example 97.4% $H_2SO_4$, is negligible, because $H_2O$ can decompose the postulated aryl pyrosulfonate intermediate which is required for sulfone formation.[7,22] However, in 100% $H_2SO_4$, where $H_2O$ is absent, some modest sulfone formation could occur. We feel fairly safe in concluding that our measurements in 97.4% $H_2SO_4$ were unaffected by any cross-linking reactions. We note that we have no direct (e.g., spectroscopic) evidence for sulfone formation. Nonetheless, it is chemically reasonable and explains otherwise puzzling results.

In order to make corrections to the apparent $\bar{M}_w$ value obtained from the Zimm plots, it was necessary to recover PEEK from the acid solutions and to analyze it for degree of sulfonation by elemental analysis ($X_E$) and titration ($X_T$). For PEEK precipitated from $H_2SO_4$, the substituents can only be $SO_3H$. However, for PEEK precipitated from $HSO_3Cl$, the initially formed $SO_3H$ groups are converted to acid chloride groups $SO_2Cl$ by the large excess of $HSO_3Cl$.[7,22] Somewhat surprisingly, even using $H_2O$ in the precipitation and workup steps, essentially none of the acid chloride groups were hydrolyzed, as evidenced by Cl/S ratios identical with the theoretical value of 1.11 which is expected for $SO_2Cl$ groups. Only if the precipitated polymer was allowed to stand in the strongly acidic supernatant did noticeable hydrolysis occur. Extent of hydrolysis was estimated from the Cl/S ratio obtained from elemental analysis, which could be combined with total substitution level $X_E$ to calculate a theoretical acid value.

Typical results are shown in Table III. For all these polymers, elemental analyses and titrations were in good agreement; however, as seen in Table III, titrations usually gave slightly higher acid values than predicted from the elemental analyses. This could be due either to a slight difficulty in seeing the end point or to small amounts of residual acid not removed by washing. Results of elemental analyses and titrations are consistent with sulfo-

**Table IV**
**Room-Temperature Solubility of Sulfonated PEEK-2**

| solvent | $X_{SO_3H}$ = 0.97 | $X_{SO_2Cl}$ = 1.26 |
|---|---|---|
| DMF | + | + |
| $Me_2SO$ | + | + |
| toluene | − | − |
| acetone | − | − |
| $CHCl_3$ | − | − |
| THF | − | −/+ |
| 95% EtOH | + | − |
| *i*-PrOH | + | − |

nation, or chlorosulfonation, of PEEK and inconsistent with the presence of unreacted physically trapped acid. Yields of thoroughly dried polymers agreed closely with those predicted from analyses.

There is strong circumstantial evidence that sulfonation of PEEK proceeds nearly exclusively at site 1 not at sites 2 or 3 (see Figure 1a) as would be predicted from consideration of substituent effects on the orientation of this aromatic substitution reaction. Limiting degree of sulfonation of PEEK in $H_2SO_4$ is seen from Table III to reach one $SO_3H$ group per repeat unit; note that there are two rings per repeat unit with sites 2 and 3, but only one with site 1. Furthermore, $^1H$ NMR of poly(oxy-1,4-phenylenecarbonyl-1,4-phenylene) (PEK), which contains only rings with sites 2 and 3, shows no evidence of sulfonation.[3] With the stronger reagent $HSO_3Cl$, apparently further substitution proceeds, most likely at site 2. The $^{13}C$ NMR spectrum of sulfonated PEEK in $Me_2SO$-$d_6$ confirms that substitution is predominantly at site 1, that is, in the phenyl ring flanked by two ethers.[33]

Solubility of polymers precipitated from $H_2SO_4$ and $HSO_3Cl$ (Table IV) is a clear indication that the recovered polymers differ substantially from virgin PEEK. It is not known how the apparent solubility of the polymers from $HSO_3Cl$ is affected by the cross-links. Dried polymers are yellow due to self-protonation of carbonyl groups.

Reiterating, evidence for sulfonation is provided by elemental analysis, titration, IR and NMR spectra, and the modified solubility of recovered PEEK. These results cannot be explained as the result of PEEK contaminated by residual unreacted acid.

All protonic acids and Lewis acids (e.g., $AlCl_3$) cause exposed polymer surfaces and dissolved polymer to turn a yellowish red. This is presumably due to strong absorption in the blue and green region of the visible spectrum. For example, in 97.4% $H_2SO_4$, $\lambda_{max}$ = 408 nm and $\epsilon_{max}$ = 169 000 cm$^3$/g-cm. This absorption is attributed to protonation of the carbonyl. Addition of $H_2O$ causes a slight blue shift with decreased absorbance (e.g., 92.2% $H_2SO_4$ has $\lambda_{max}$ = 406 nm and $\epsilon_{max}$ = 147 000 cm$^3$/g-cm). The exact features of UV–vis spectra depend in complicated ways on acid strength, method of solution preparation, time after mixing, concentration, and sample. The dispersion of d*n*/d*c* appears also to be related to the absorption phenomenon. Figure 5 shows representative absorption spectra and d*n*/d*c* dispersion.

Absorption in the range of interest for scattering, say 500–650 nm, is far stronger and increases more with time for solutions of PEEK in $HSO_3Cl$ than in $H_2SO_4$. In fact, after a week, scattering experiments on $HSO_3Cl$ solutions of PEEK became impractical using the 514.5-nm Ar laser, due to extremely low signal caused by attenuation of the beam. In contrast, in 97.4% $H_2SO_4$, the absorption at longer wavelength remains essentially constant with time, at a far lower level. Typically $\epsilon$ = 10 cm$^3$/g-cm ($H_2SO_4$, 632.8 nm), whereas $\epsilon$ = 100 cm$^3$/g-cm ($HSO_3Cl$, 632.8 nm). One might speculate that increasing absorption for PEEK in $HSO_3Cl$ at longer wavelength is correlated with the increase in sulfone cross-links or the increase in chlorosulfonation.

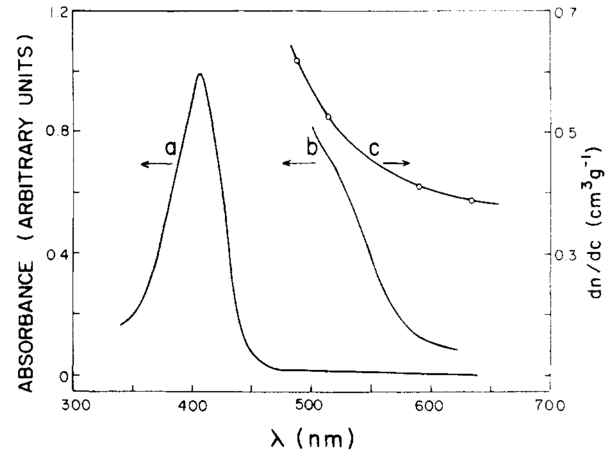

**Figure 5.** (a) Absorbance of a dilute (8 ppm) solution of PEEK-2 in 97.4% $H_2SO_4$. Full scale = 0.54 AU. (b) Absorbance of a concentrated (7 mg/mL) solution of PEEK-1. Full scale = 1.0 AU. (c) Dispersion of refractive index increment (d*n*/d*c*) for PEEK in 97.4% $H_2SO_4$.

**Table V**
**Solubility of PEEK at 25 °C**

| solvent | solubility |
|---|---|
| 94.9% $H_2SO_4$ | complete |
| 89.9% $H_2SO_4$ | nearly complete |
| 84.8% $H_2SO_4$ | partial |
| 79.6% $H_2SO_4$ | negligible |
| $CH_3SO_3H$ | complete |
| $CF_3CO_2H$ | negligible |
| poly(phosphoric acid) (100 °C) | slight/partial |

Solubility of PEEK in various acids not mentioned thus far is shown in Table V. Presumably, protonation of PEEK gives rise to repulsive electrostatic forces which can overcome the strong attractive forces in this highly crystalline polymer. Concurrent sulfonation, observed to occur in $H_2SO_4$ and $HSO_3Cl$, but not in $CH_3SO_3H$, may aid in solubilizing the polymer by further disrupting the structure. In aqueous $H_2SO_4$, as acid strength and associated protonating and sulfonating powers decrease, observed solubility also decreases dramatically. Poly(phosphoric acid) (PPA) at 100 °C was found by us to only partially dissolve PEEK, whereas previous workers[3] reported PPA to be a solvent for structurally similar PEK. The difference in results might be ascribed to higher charge density in protonated PEK compared to PEEK, to lower degree of polymerization of PEK, or to the fact that PPA was present from the start of the PEK polymerization reaction, so that the PPA was not required to dissolve an already crystalline polymer. $CF_3CO_2H$ did not dissolve PEEK. We did not examine liquid HF, which has previously been employed as a reaction solvent.[2] Only at temperatures approaching the melting point of the polymer (335 °C) can solvents dissolve PEEK without protonation and/or chemical modification, with the best solvent found to be the structurally similar diphenyl sulfone.[4]

This study has shown possible dangers which may arise in characterizing polymers which dissolve only in strong acids. The nature of the dissolved polymer, dependent on protonation and insome cases chemical modification, which are both in turn intimately related to the nature of the particular solvent, must always be kept in mind.

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**Registry No.** $H_2SO_4$, 7664-93-9; $HSO_3Cl$, 7790-94-5; PEEK, 31694-16-3.

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# Computer Simulation of Three-Dimensional Multiple-Chain Systems: Scaling Laws and Virial Coefficients

**Hans Christian Öttinger**

*Fakultät für Physik der Universität Freiburg i.Br., D-7800 Freiburg i.Br., West Germany.*
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ABSTRACT: The "scanning method" which has recently been developed for the Monte Carlo simulation of single polymer chains is applied to multiple-chain systems on a simple cubic lattice. By this method the partition function of the multiple-chain system can be estimated directly. Therefore a scaling law for the partition function which is equivalent to des Cloizeaux's famous scaling law for the osmotic pressure can be tested. Furthermore, the second and third virial coefficients can be extracted from the Monte Carlo data. The compatibility of the results with the scaling law for the osmotic pressure is discussed.

## 1. Introduction

In recent years the experimental and theoretical investigation of polymer solutions at moderate concentrations has made great progress.[1] A great deal of the theoretical investigations—especially Monte Carlo simulations—is based on the self-avoiding walk (SAW) model of polymer chains. In this lattice model the macromolecules are represented by chains of sites occupied by monomers and connected by links of the underlying lattice. All allowed multiple-chain configurations are equally probable, and the only interaction results from the condition that double occupancy of lattice sites is forbidden (excluded volume). One can assume solvent molecules to be attached to the lattice sites which are not occupied by monomers.

Despite the simplicity of the SAW model a lot of experimental results[2,3] for athermal solutions—these are solutions in good solvents for which only entropy effects are present—can be explained by this model very well. In particular, the SAW model includes the universal scaling laws[4–6] predicted by field-theoretic methods and confirmed by experimental results. The most important one is des Cloizeaux's scaling law for the osmotic pressure of polymer solutions which will be tested in the present paper by Monte Carlo simulation of multiple-chain systems on a five-choice simple cubic lattice.

In the next section the scaling law for the osmotic pressure will be transcribed into an equivalent scaling law for the partition function. This will be done because the partition function can be estimated directly by the "scanning method" which has recently been developed by Meirovitch[7,8] for the Monte Carlo simulation of single polymer chains. In the third section the scanning method applied in the present paper to the simulation of multiple-chain systems will be described in detail. The results of the Monte Carlo simulation will be presented in the fourth section. Besides the scaling function for the partition function the second and third virial coefficients will be estimated, and the unsettled question about the validity of des Cloizeaux's scaling law in three dimensions will be discussed. A brief summary concludes the paper.

## 2. Scaling Laws

The most important result gained by the application of field-theoretic methods to polymer solutions is the scaling

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