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Kinetics of PEEK Sulfonation in Concentrated Sulfuric Acid[†]

Nobuhiro Shibuya[1] **and Roger S. Porter***

Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003

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ABSTRACT: The sulfonation kinetics of poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (PEEK) was studied in 96.3% sulfuric acid. The reaction rate was found to be first order and inversely first order with respect to the PEEK and the sulfonated PEEK chain repeat unit, respectively. The latter results from desulfonation taking place in this system, rather than an inhibition caused by the water produced. The reaction progress at three PEEK concentrations, 0.02, 5.0, and 20 g of PEEK/sulfuric acid, is in agreement, indicating an absence of the effect of the initial PEEK concentration. The reaction follows the Arrhenius equation over the temperature range of study, 25–75 °C with a calculated activation energy of 20.4 kcal/mol of repeat unit, within the range of related reports.

Introduction

The kinetics of arylsulfonation have been studied since 1908.[2] Most studies before 1969 have been summarized by Cerfontain[3] and by Taylor.[4] Chemical Abstracts reveals many subsequent reports for the rates and the activation energies of low molecular weight organics sulfonation. The following brief review serves to reintroduce the fundamentals of sulfonation for polymer studies.

Kinetic Expressions. The following equation has widely been used to express arylsulfonation in aqueous sulfuric acid:

$$-\frac{d[\mathrm{Ar}]}{dt} = k[\mathrm{Ar}][\mathrm{H_2SO_4}]^2/A_w \qquad (1)$$

wherein [Ar] = concentration of the aromatic ring to be sulfonated, $[H_2SO_4]$ = concentration of sulfuric acid, and A_w = activity of water in the system. The second order of the acid concentration and the inverse term of the water activity have been rationalized by a reaction of two H_2SO_4 molecules producing the sulfonation species.

For Sulfonation of Small Molecules with Sulfuric Acid. Sulfonation of benzene,[5] toluene,[6] *p*-xylene,[7] *tert*-butylbenzene,[8] ethylbenzene,[9] and isopropylbenzene[10] has been reported. Most studies show that the reaction rate is proportional to the aromatic ring concentration.

Solvent in the sulfonation system has been reported not to affect the rate equation.[11–15] The sulfonation rate of benzene by sulfuric acid in nitrobenzene[11,12] and in dimethyl sulfate[13] of toluene in nitrobenzene,[11,14] and of biphenyl in nitrobenzene[15] has been shown to be first order with respect to the aromatic ring concentration, consistent with eq 1.

Strong acids have been known to facilitate the desulfonation of arylsulfonic acids.[3] In spite of the presence of trifluoroacetic acid, the sulfonation rate of benzene with sulfuric acid has been reported to be first order with respect to the concentration of the substrate but a coexistence of the desulfonation has not been reported.[16]

Although arylsulfonation is known to be reversible, the presence of the arylsulfonic acid at the beginning of the reaction has not been reported to affect the order of the rate equation. The sulfonation of benzene with sulfuric acid is first order with respect to the substrate concentration in aqueous benzenesulfonic acid.[17]

Sulfonation of Polymers. Akovali and Özkan studied the sulfonation kinetics of polystyrene in sulfuric acid and found that only the para position of the phenyl ring was sulfonated.[18] The rate was treated as first order with respect to the polystyrene repeat unit.

The sulfonation of cross-linked polystyrene beads swollen with 1,2-dichloroethane in sulfuric acid has been reported by Wiley and Venkatachalam.[19,20] They treated the kinetic data as first order with respect to the polystyrene repeat unit and showed that the rate was affected by a diffusion of the sulfuric acid in the polymer matrix.

Bailly et al. studied the sulfonation of poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (PEEK) in concentrated sulfuric acid and in the mixture of the acid and methanesulfonic acid at room temperature.[21] They reported that the sulfonation level was a function of the fourth power of the sulfuric acid concentration but did not provide a rate equation. The rate-slowing effect of the solvent methanesulfonic acid was explained as dilution, solvation, and a reaction with sulfonating species and their precursors.

Activation Energy and Characteristics of the Reaction. The rates of sulfonation have been measured at different temperatures to provide the energy of reaction activation (E_a). The E_a for the sulfonation of small aromatic molecules has been reported to be from 6[11] to 47 kcal/mol.[22]

The concentration of sulfuric acid is known to affect the E_a.[3,4] For the sulfonation of benzene in aqueous sulfuric acid, the E_a systematically changes from 25.2 to 18.0 kcal/mol in the range of the acid concentration from 77.6% to 95.9%.[5] In contrast, the E_a (22.6 ± 1.1 kcal/mol) for *p*-xylene sulfonation does not change for a concentration of sulfuric acid from 72.3% to 89.1%.[7] In this case, steric hindrance may possibly affect the reaction. The choice of solvent in the sulfonation system was reported to result in a different E_a. For benzene sulfonation with sulfuric acid (99.6–100%), the E_a in nitrobenzene was 7.5 kcal/mol[11] and the E_a in dimethyl sulfate was 8.4 kcal/mol.[13]

The sulfonation study of cross-linked polystyrene beads swollen with 1,2-dichloroethane in sulfuric acid showed an E_a dependent on the degree of cross-linking.[19] The more cross-linked the polymer, the higher E_a, considered due to the slow diffusion of the acid in the hindering matrix of the polymer.

PEEK (ICI:Victrex PEEK) is a semicrystalline polymer with good mechanical properties, high thermal stability,

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* To whom all correspondence should be addressed.

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and chemical resistance. Chemical modification of this polymer has been of wide interest, for example, sulfonation,[21,23,24] formation of ionomer through sulfonation,[21,23] nitration,[25] amidation,[25] and sulfamidation.[25]

In this paper, the kinetics of PEEK sulfonation in concentrated sulfuric acid is studied to show the characteristics of this system.

Experimental Section

Materials. Poly(ether ether ketone) (PEEK) powder was generously provided by ICI America Inc., Wilmington, DE. The PEEK (ICI grade 380P: batch no. PB/64, M_n = 14 100, M_w = 38 600) was dried at 150–160 °C for 5 h in vacuo and then cooled to room temperature in a desiccator prior to use. The PEEK powder was previously sieved not to contain large (>1 mm) particles. The results of the elemental analysis were as follows:

	measd wt %	calcd wt %
carbon	79.03	79.16
hydrogen	4.16	4.20
sulfur	0.29	0.00

The trace of sulfur was derived from the residue of diphenyl sulfone used as solvent in polymerization.[21] The powder contained ash (0.4 wt %) as reported by the producer. The amounts of these impurities are so small that they do not significantly affect the kinetic measurement.

Sulfuric acid (Fisher Scientific, ACS grade, concentration 96.3 wt % reported by the supplier) was used without further purification.

The water used for sulfonated sample precipitation and washing was deionized (electric resistance > 1 MΩ).

General Procedure of Sulfonation and Kinetic Measurements by Elemental Analysis. PEEK powder was dissolved in sulfuric acid (96.3%) to form 5.00 and 20.0 g/L solutions. The solutions were made by vigorous stirring in a three-necked flask with a sealed mechanical stirrer, a drying tube, and a thermometer. The flask was put in a thermostated oil bath and kept at a set temperature (±1 °C). The reaction mixture became transparent on dissolution. The reaction time range was 1–100 h. A 30-mL aliquot for the 5.00 g/L solution or a 10-mL aliquot for the 20.0 g/L solution was taken from the reaction mixture at fixed times and quenched by cooling to 0 °C in an ice-water bath. The aliquot removal was done quickly and carefully to exclude moisture contamination which can affect the reproducibility and extent of sulfonation. The sulfonated samples were recovered by a precipitation process. The precipitation was performed by dropwise addition of the aliquot into four parts of the deionized water at 0 °C. The sample mixture was filtered and washed with the deionized water more than three times to remove the remaining sulfuric acid and until the wash water was neutral. For the very hygroscopic samples, i.e., for sulfonation of more than 0.8 (per mole of repeat unit), twice- or thrice-washed precipitate became a gel, which could not be easily washed and slowly dissolved in the washing water. To remove the remaining sulfuric acid from these samples, the following method was applied. The gel was dissolved in a minimal amount of ethanol (95%). The solution was evaporated, and the sample was dried in vacuo, at room temperature, resulting in a thin film. This film was washed with deionized water successively until the wash water was neutral. The washed film samples were dried in vacuo at 100–105 °C for 4 days and then stored in a vacuum desiccator over calcium sulfate. Elemental analysis of the samples was performed by the University of Massachusetts Microanalysis Laboratory. The degree of sulfonation (X) was determined from the sulfur-to-carbon ratio.

Procedure for the Kinetic Measurements by UV–Visible Spectroscopy. Precisely weighed PEEK (2.17 mg) was dissolved in 96.3% sulfuric acid (100 mL) and stirred vigorously at 35 °C (±1 °C) in a three-necked flask with a magnetic stirrer, a thermometer, and a drying tube. The flask was placed in an oil bath with a thermostat. A solution aliquot (~2.5 mL) was taken from the reaction mixture using a pipet at set times. The sample aliquot was quickly moved into a quartz cuvette on an ice-water bath to undergo UV–visible spectroscopic measurement. After the 50-h measurement, the reaction mixture was heated to 75 °C and kept for 24 h to obtain the absorption of entirely sulfonated PEEK (reaction ending point). The absorption intensity became constant on heating at 75 °C for longer than 5 h.

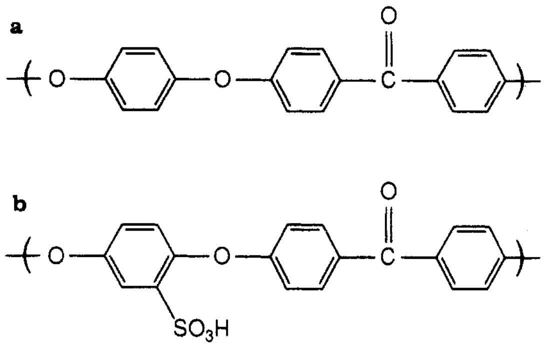

Figure 1. Chemical structure of PEEK (a) and a sulfonated PEEK (b) repeat unit.

Sample Analysis and Characterization. UV–visible absorbance spectra were measured at room temperature using a Beckman UV-7 spectrophotometer. The measurement was performed from 320 to 335 nm, at a 120 nm/min scanning rate. The scans were repeated more than five times to obtain precise averages. The band observed at 326–327 nm is due to the sulfonated phenyl ring flanked by two ether groups. The peak absorption intensity systematically increased with reaction time. The extent of sulfonation (X) was calculated from the following ratio as $X = (I - I_0)/(I_e - I_0)$, wherein I, I_0, and I_e stood for the absorption intensity of the measuring time, of the reaction starting point, and of the reaction ending point ($t = \infty$), respectively. This procedure has been detailed.[26]

Carbon-13 NMR spectra measurement was performed using a Varian XL-200 spectrometer with broad-band proton decoupling at 60 °C. The polymer solution was 5% (w/v) in DMSO-d_6; the solvent carbon peak at 39.6 ppm is a reference (the solvent peak position relative to tetramethylsilane). Infrared spectra of the samples were measured using a Perkin-Elmer 1320 infrared spectrophotometer.

Results and Discussion

The chemical structure of sulfonated PEEK samples was evaluated by comparison of the carbon-13 NMR and the infrared spectra with reported data.[23] The degree of sulfonation was calculated from elemental analyses and UV–visible spectroscopy. The chemical repeat unit is shown in Figure 1. Jin et al. reported that sulfonation takes place only on the phenyl ring flanked by two ether groups of the PEEK repeat unit.[23] This phenylene ring has four equivalent ortho positions for sulfonation, with only one of the four protons on the ring being substituted in concentrated sulfuric acid at ambient temperature.[23] The other two phenyl rings, connecting an ether group and a carbonyl group, are deactivated for the electrophilic sulfonation by the electron-withdrawing effect of the carbonyl group. Further sulfonation (more than one) on the same phenyl ring is not expected to occur under the condition of this study, because of the electron-withdrawing effect of the introduced acid group. Indeed, the degree of sulfonation was limited to 1, within an experimental error of ±2%, for the reaction at 75 °C for 5–10 h. Bishop et al. also reported that the degree of sulfonation is 1 in 97.4% sulfuric acid at room temperature for times up to 33 days.[24]

The sulfonation kinetics in 96.3% sulfuric acid was measured at four constant temperatures from 25 to 75 °C. The results are given in Figure 2. The rate gradually slows with reaction time. Temperature significantly increases the rate. The origin of the time scale is set at an approximate time of the entire dissolution. For the

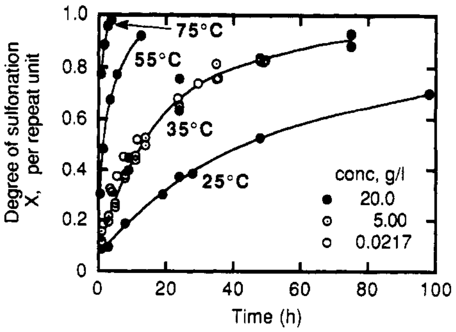

Figure 2. Kinetics of PEEK sulfonation in sulfuric acid (96.3%). X represents the degree of sulfonation per repeat unit. The origin of the time scale is from the onset of complete dissolution.

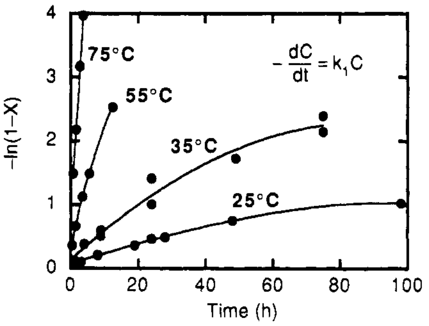

Figure 3. Kinetics of PEEK sulfonation in sulfuric acid: the first-order rate treatment with respect to the substrate concentration. X represents the degree of sulfonation per repeat unit. The origin of the time scale corresponds to a time after the entire dissolution.

experiments at 20.0 g/L, these times were around 2, 1, 0.5 and 0.25 h at 25, 35, 55, and 75 °C, respectively. PEEK is said to dissolve in strong acid such as sulfuric acid, as the result of protonation on the carbonyl groups and the phenyl rings.[24] The polymer may be sulfonated in a small part while it is going into solution.

The reaction kinetics were measured at three levels of initial PEEK concentration (20.0, 5.00, and 0.0217 g/L) at 35 °C to examine the effect of concentration. For these experiments, the reaction progress is found to be in agreement within experimental error, as given in Figure 2. This indicates that the reaction is not affected by polymer–polymer interchain interaction. In the figure, the origin of the time scale is again set at an approximate time of the entire dissolution. Complete dissolution of the polymer took around 30 min and 1 h for the reactions at 0.0217 and 5.00 g/L, respectively.

The initial PEEK concentrations were set at relatively low levels, up to 20.0 g/L, to keep the sulfuric acid concentration nearly constant during the reaction, since the water produced by sulfonation can dilute the acid and slow the reaction.[3,4] For the experiments at 20.0 g/L, the amout of water equivalent for complete sulfonation was estimated to be 1.25 g, which is 1.85 wt % of the initial amount of water (67.7 g) in 1 L of the sulfuric acid. The water was calculated to reduce the acid concentration by 0.1%. This difference is thought to be negligible for the kinetic measurement.

Data and Kinetic Expression. The rate of aromatic sulfonation has been reported to be first-order, proportional to the phenyl ring concentration at a nearly constant concentration of sulfuric acid.[3-20] Use of low concentrations of the substrate and the small amount of water produced by the reaction did not contribute significantly to the acid concentration in the reaction mixture. Here, the repeat unit is regarded as a small aromatic molecule for the kinetic treatment, and thus the degree of sulfonation (X) can be considered to be equivalent to the reaction conversion.

If the rate of the reaction is first order with respect to the substrate phenyl ring, the rate equation is described as

$$-\mathrm{d}C/\mathrm{d}t = k_1C \qquad (2)$$

wherein C and k_1 represent the substrate concentration and the first-order rate constant, respectively. This equation is integrated from the beginning of the reaction ($C = C_0$ at $t = 0$) to a concentration ($C = C_0$ at $t = t$) to give eq 3.

$$-\ln (C/C_0) = k_1t \qquad (3)$$

The concentration of the substrate is described as

$$C = C_0(1 - X) \qquad (4)$$

wherein X stands for the sulfonation degree per repeat unit. X is equal to zero at the beginning of the reaction and equals 1 at the end of the reaction. C in eq 3 may be substituted by eq 4 to give

$$-\ln (1 - X) = k_1t \qquad (5)$$

If the rate is first order with respect to the substrate concentration, a plot of $-\ln (1 - X)$ vs time will fit a straight line. Curvature in Figure 3 shows that the reaction rate is not first order. Data simulate a linear function only at an early stage of the reaction, which is the first-order rate region. The rate subsequently becomes slower than first order, with the difference between the data and a straight line gradually increasing as the reaction progresses. This tendency suggests that factors slow (deflate) the reaction.

Deflator Derived from the Product and Rate Expression. If the reaction deflator is derived from the product or is the product, it would appear as an inverse term in the rate equation as

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{k_1C}{k_\mathrm{d}(C_0 - C)} \qquad (6)$$

wherein k_d represents the rate constant of the inhibition or the reverse reaction. Equation 6 is integrated from C_0 to C to give eq 7a and an integration gives

$$-\int_{C_0}^{C}\frac{C_0 - C}{C}\,\mathrm{d}C = \frac{k_1}{k_\mathrm{d}}\int_0^t\mathrm{d}t \qquad (7a)$$

$$-\frac{C_0 - C}{C_0} - \ln\frac{C}{C_0} = \frac{k_1}{k_\mathrm{d}}\frac{1}{C_0}t \qquad (7b)$$

Equation 7b is redefined as a function of X by substitution of eq 4 to give eq 7c. The k_1/k_d was calculated from the

$$-X - \ln (1 - X) = \frac{k_1}{k_\mathrm{d}}\frac{1}{C_0}t \qquad (7c)$$

slope obtained from the least-squares fit of the plots. Values calculated through eq 7c are plotted vs time in Figure 4. The points fall on a straight line. This is consistent with the reaction being distinctly affected by a deflator derived from the reaction product.

Rate Expression and Deflator Derived from Substrate. If the reaction intermediate consists of two substrate molecules, the effect can appear as an additional power of substrate concentration in the rate expression. In this case, the known equation is

$$-\mathrm{d}C/\mathrm{d}t = k_2C^2 \qquad (8)$$

wherein k_2 represents the second-order rate constant.

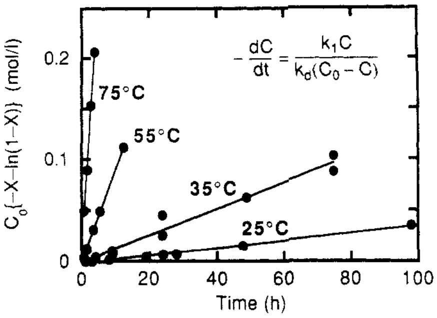

Figure 4. Kinetics of PEEK sulfonation in sulfuric acid: $C_0\{-X - \ln(1 - X)\}$ vs reaction time. X stands for the degree of sulfonation per repeat unit. The origin of the time scale is from the onset of complete dissolution.

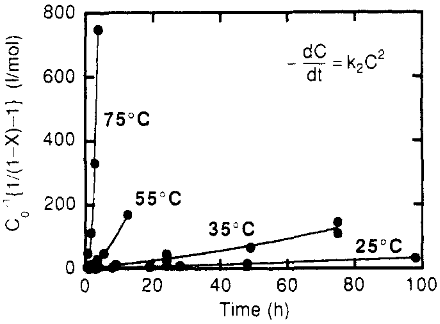

Figure 5. Kinetics of PEEK sulfonation in sulfuric acid: the second-order rate treatment with respect to the substrate concentration. X represents the degree of sulfonation per repeat unit. The origin of the time scale corresponds to a time after the entire dissolution.

Equation 8 integrates from C_0 to C to give eq 9. C in eq 9 is substituted by eq 4 to give

$$\frac{1}{C} - \frac{1}{C_0} = k_2t \tag{9}$$

$$\frac{1}{1-X} - 1 = C_0k_2t \tag{10}$$

The data calculated through eq 10 are plotted in Figure 5. The data are not collinear; an exception may be in the data at 75 °C which is insensitive. These results are consistent with an absence of an intermediate consisting of two substrate repeat units.

Meaning of the Product Deflator. 1. Desulfonation. From results here, desulfonation is thought to be the origin of the deflator in PEEK sulfonation for the following reason. Sulfonation of aromatic compounds is known to be reversible.[3] Arylsulfonic acids can be desulfonated in the presence of acid or water.[3,11] Sulfonated PEEK readily desulfonates to give PEEK in methanesulfonic acid.[28] Some reports on arylsulfonation emphasize the existence of sulfonation–desulfonation equilibria in sulfonation systems.[11,21,27] Of course, steric and electronic effects may contribute to the reverse reaction.[3] A cross-linking formed by sulfone formation between two sulfonated PEEK chains is not considered to occur: A gel or an insoluble portion was not found in the ethanol, the dimethylformamide, or the dimethyl sulfoxide solutions of the PEEK completely sulfonated at 75 °C ($X = 1.0$). The sulfone cross-linking of PEEK has not been observed in 97.4% sulfuric acid at room temperature.[24]

2. Effect of Water as a Byproduct of Sulfonation. An equivalent amount of water is produced as the result of sulfonation, which dilutes sulfuric acid in the reaction mixture. The relative concentrations were chosen so that this water will make no contribution to the reaction. In the experiments at 0.0217, 5.00, and 20.0 g/L of initial PEEK concentration, the molar equivalent waters produced by complete sulfonation are 1.36×10^{-3}, 0.312, and 1.25 g, respectively. These amounts are considered to be insignificant compared to the initial concentration of water (67.7 g) in 1 L of the sulfuric acid used.

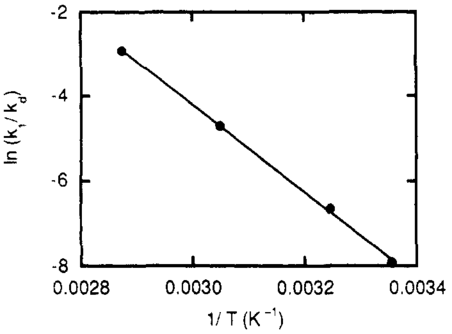

Figure 6. Arrhenius plot of the rate constant ratio (k_1/k_d) as $\ln(k_1/k_d) = -1.03 \times 10^4/T + 26.6$; correlation coefficient (R) = 0.9996.

The reaction at 35 °C progress at the three concentrations of PEEK is in agreement within experimental error, as given in Figure 2. Kinetic data at 25 °C agree with that reported at room temperature by Bailly et al.[21] In their experiment, the initial concentration of PEEK was 100 g/L in 96.4% sulfuric acid. The concentration of sulfuric acid is estimated to have changed from 96.4% to 96.0%. The data consistence confirms that the rate is insensitive to the sulfuric acid concentration in this range.

The water generated (1.25 g) is calculated to reduce the sulfuric acid concentration from 96.3% to 96.2%. The difference of the acid concentration for the experiments at 35 °C is calculated to be 0.1% or less. The concentration of the sulfonation entity vs sulfuric acid concentration has been reported by Cerfontain et al.[3,5] Their data imply that the difference (≤0.1%) of the acid concentration around 96.3% is too small to significantly change the concentration of sulfonation species and the rate. It is thus not possible to attribute the rate deflation to the water or to the water activity (A_w) in eq 1.

Arrhenius Plot and Activation Energy (E_a). An Arrhenius plot for the sulfonation of PEEK is given in Figure 6, which shows that the reaction fits this form from 25 to 75 °C. This is consistent with an absence of any major side reaction.

An E_a of 20.4 kcal/mol of repeat unit was calculated from the slope obtained from the least-squares fit of the plots. This value is within the range of data (18–23 kcal/mol) reported for sulfonation of aromatic hydrocarbons in 89–97% sulfuric acid.[5-8]

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