

A kinetic study of PEEK sulfonation in concentrated sulfuric acid by ultraviolet-visible spectroscopy

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The sulfonation kinetics of poly(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene) (PEEK) has been studied at highly dilute conditions ($\sim 0.02 \text{ g l}^{-1}$) in 96.3% sulfuric acid. The sulfonation was observed from 35 to 75°C using ultraviolet-visible spectroscopy. The fractional sulfonation has been calculated from the ratio, $I - I_0 / I_\infty - I_0$, where I , I_0 and I_∞ represent the spectral absorption of the reaction system at a time t , at the starting point and at the ending point, respectively. The I_0 is extrapolated from a least-squares plot of the data calculated through a kinetic equation combined with the ratio cited above. The reaction rate was confirmed to be first order in the PEEK chain repeat unit and also inversely first order with respect to the concentration of the sulfonated PEEK repeat unit. The reaction follows the Arrhenius equation over the temperature range of study, with a calculated activation energy of 82.8 kJ mol^{-1} repeat unit. Good agreement has been obtained between these results and the data measured in a more concentrated system (20 g PEEK/l H_2SO_4).

(Keywords: PEEK; sulfonation; kinetics)

INTRODUCTION

Despite a considerable history, curiosities and inconsistencies still remain concerning the kinetics of arylsulfonation by sulfuric acid (H_2SO_4). To extend and resolve prior publications, we have conducted additional sulfonation tests of an arylpolymer and evaluated the results by a sensitive and selective spectroscopic technique. The arylpolymer chosen, PEEK (ICI: Victrex PEEK), is semicrystalline and possesses good mechanical properties, high thermal stability and chemical resistance. Sulfonation¹⁻³ and some other chemical modifications²⁻⁴ of this polymer have been of interest. Jin *et al.*² evaluated the chemical structure of PEEK sulfonated in concentrated H_2SO_4 and reported that sulfonation occurs only on a phenyl ring flanked by two ether groups (A-ring) of the PEEK repeat unit, as shown in Figure 1. The A-ring has four equivalent *ortho* positions to be sulfonated, with only one of the four protons on the ring being substituted in concentrated H_2SO_4 at ambient temperature². Further sulfonation (more than one) on the A-ring does not occur under the condition, because of the electron-withdrawing effect of the acid group. The other two phenyl rings connecting with an ether group and a carbonyl group are deactivated to the electrophilic sulfonation by the electron-withdrawing effect of the carbonyl group. Indeed, the fractional sulfonation is limited to one per repeat unit, up to 75°C in concentrated H_2SO_4 ^{1,5,6}. We have studied the kinetics of PEEK sulfonation in

concentrated H_2SO_4 at higher concentration (20 g l^{-1})^{5,6}. It was found that the rate is not only first order with respect to the PEEK repeat unit concentration, but also inversely first order with respect to the concentration of the sulfonated PEEK repeat unit^{5,6}. The conclusion was that the inverse term resulted from a retardation based on the product, i.e. a competing desulfonation. This result is different from that in former reports for the arylsulfonation of low molecular weight organics, in which the rate is first order with respect to the aryl ring to be sulfonated^{7,8}. A study of PEEK sulfonation in highly dilute conditions seems to be required as a more rigorous evaluation of the retardation reaction to evaluate the prior conjecture concerning retardation. For reasons that follow, a sulfonation analysis based on ultraviolet-visible (u.v.-vis.) spectroscopy has been expected to be suitable for this purpose.

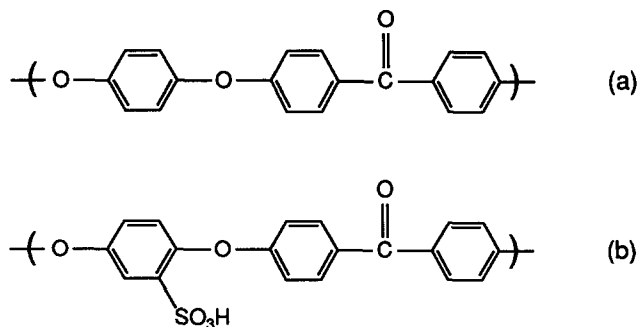


Figure 1 Chemical structure of PEEK (a) and sulfonated PEEK (b) repeat units

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U.v.-vis. spectroscopy is an efficient method to quantitatively analyse compounds possessing a multiple bond, such as an aromatic structure. The spectroscopy has been widely applied to kinetic studies⁹⁻¹¹, since the simple and fast measurements can give accurate, precise and direct analyses of reaction mixtures. Generally, the u.v.-vis. spectra of aryl compounds are measured in highly dilute conditions (10 mg l⁻¹, for example) because of the compounds' large absorption coefficients ($\epsilon_{\max} = 10^3-10^6$ l/mol cm)¹². Indeed, this condition is suitable for the analysis of arylsulfonation. The reaction produces arylsulfonic acid and water. The water produced dilutes H₂SO₄ and slows the reaction^{7,8}. In highly dilute solution, the number of water molecules produced by the reaction is negligible compared with the original amount of the acid and water, and thus may be considered to have an insignificant effect on the rate.

For the measurement of reaction progress, the fractional sulfonation (X) per chain repeat unit is calculated from the following ratio:

$$X = (I - I_0)/(I_\infty - I_0) \quad (1)$$

where I , I_0 and I_∞ represent the absorbances at a time t , at the reaction starting point ($t=0$) and at the reaction ending point ($t=\infty$). I_0 cannot be measured directly because the absorption changes during the dissolution (about 1 h at 35°C) due to the concurrent reaction of PEEK and H₂SO₄. It thus must be measured or estimated by another method, because of the reactivity and the slow dissolution of the polymer. The uncertainty in I_0 is overcome by a combination of kinetic equations and a statistical treatment of data in this paper. The results are compared with the kinetic data measured in a relatively concentrated system (20 g l⁻¹)^{5,6}, to evaluate previous kinetic results in terms of the retardation caused by the sulfonated PEEK repeat unit.

EXPERIMENTAL

Materials

Poly(ether ether ketone) (PEEK) powder was generously provided by ICI America Inc., Wilmington, DE, USA. The PEEK (ICI grade 380P: batch no. PB/64, $M_n = 14\,100$ g mol⁻¹, $M_w = 38\,600$ g mol⁻¹) was dried at 150–160°C for 5 h *in vacuo* and then cooled to room temperature in a desiccator over calcium sulfate, prior to use. The PEEK powder had been sieved to exclude large particles (> 1 mm). The results of elemental analysis were as follows. Measured (wt%): C 79.03, H 4.16, S 0.29; calculated (wt%): C 79.16, H 4.20, S 0.00. The trace of sulfur was derived from the residue of diphenyl sulfone which had been used as solvent in polymerization³. The powder contained 0.4 wt% ash, as reported by the producer. These impurities are considered to have an insignificant effect on the kinetic measurements.

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 (electrical resistance > 1 M Ω).

General procedure for kinetic measurements by u.v.-vis. spectroscopy

Precisely weighed PEEK (1.9–2.3 mg) was dissolved in 96.3% H₂SO₄ (100 ml) and stirred rigorously at a set

temperature ($\pm 1^\circ\text{C}$) in a three-necked flask with a magnetic stirrer, a thermometer and a drying tube. The flask was placed on an oil bath with a thermostat at a preset temperature. A solution aliquot (~ 2.5 ml) was taken from the reaction mixture using a pipette at a series of set times. These aliquots were quickly moved into a quartz cuvette on an iced water bath. The solution-containing cuvette with a lid was shaken gently for 2 min on the cooling bath to slow the reaction. The u.v. measurement was performed within 1.5 min just after the cooling. The reaction rate below room temperature was estimated to be too slow to significantly affect the measurement of the sulfonation degree, estimated from the Arrhenius plot of the authors' former sulfonation study^{5,6}. The reaction progress was indeed found to be negligible during the cooling (2 min) and u.v.-vis. measurement within 1.5 min. After the samplings, the reaction mixtures were heated to 75°C and kept for 24 h to ensure the absorption of the reaction ending point (I_∞ , at $X \approx 1.0$). The absorbance became constant after 5 h on heating at 75°C, corresponding to complete sulfonation of one phenyl ring per repeat unit.

Preparation and characterization of a fully sulfonated PEEK for a reference

PEEK was sulfonated in H₂SO₄ (96.3%) at 75°C for over 5 h. The procedures of sulfonation, purification and characterization have been detailed elsewhere^{5,6}. The fractional sulfonation per repeat unit (X) was 1.0 (± 0.02), confirmed by the sulfur-to-carbon ratio of the elemental analyses. The chemical structure was evaluated by i.r. and ¹³C n.m.r. and compared with the reported data².

Sample analysis and characterization

U.v.-vis. spectra were measured at room temperature using a Beckman UV-7 spectrophotometer, in an absorbance mode. The response is proportional to the number of the absorbing molecules, determined by the Lambert-Beer law¹³:

$$\text{absorbance} = \epsilon cb \quad (2)$$

where ϵ , c and b are the molar absorptivity, concentration of solute and path length through the sample solution, respectively. The kinetic measurement of absorption was performed from 320 to 335 nm, at a scanning rate of 120 nm min⁻¹. The measurement was repeated five times to obtain a precise average, all done within 1.5 min. The band at 326–327 nm is due to the sulfonated phenyl ring flanked by two ether groups and protonated carbonyl group of the PEEK repeat unit. The absorbance peak gradually increased with the reaction time. The peak height was recorded as time function to follow sulfonation. The H₂SO₄ used showed no strong absorption in the 200–500 nm region.

RESULTS AND DISCUSSION

The u.v.-vis. spectra of PEEK and related compounds in H₂SO₄

The u.v.-vis. spectral data of 96.3% H₂SO₄ solution of PEEK heated at 75°C became constant for longer than 5 h. This indicates that the sulfonation is completed ($X = 1.0$) under the condition. The spectrum of the solution stirred at 75°C for 6 h is given in Figure 2, showing strong absorptions at 408 nm ($\epsilon_{\max} = 4.04 \times 10^4$ l cm⁻¹ mol⁻¹

repeat unit), 327 nm ($\epsilon_{\max} = 1.11 \times 10^4$), around 293 nm ($\epsilon_{\max} \approx 0.7 \times 10^4$) and 234–245 nm ($\epsilon_{\max} \approx 1.1 \times 10^4$). This spectrum and that of the sulfonated PEEK ($X = 1.0$) in 96.3% H_2SO_4 solution (0.0250 g l^{-1}) were equivalent. This confirms that the sulfonation gives the same chemical structure at both concentrated (20 g l^{-1}) and highly dilute ($\sim 0.02 \text{ g l}^{-1}$) conditions, as shown in Figure 1.

At the early stage of the sulfonation, the absorptions of PEEK in 96.3% H_2SO_4 can be attributed mainly to the protonated ketone group flanked by two phenyl rings, since the band positions and the intensities are similar to those reported for the diphenylketone structures of related organics. The spectral data of PEEK at 35°C for ~ 1 h in 96.3% H_2SO_4 showed absorptions at 420, 327 and around 240 nm, as given in Figure 2. These data resemble those of di-*p*-anisylketone and of di-*p*-tolylketone in 95% H_2SO_4 ¹⁴. The differences in the band positions and intensities are not significant and can be attributed to the effect of the substituents¹⁴. The absorptions of A-ring partially hide in the strong absorptions of the diphenylketone group for H_2SO_4 solution spectra. Nonetheless, a band, which grows as the sulfonation progresses, may thus be assigned to the A-ring sulfonated.

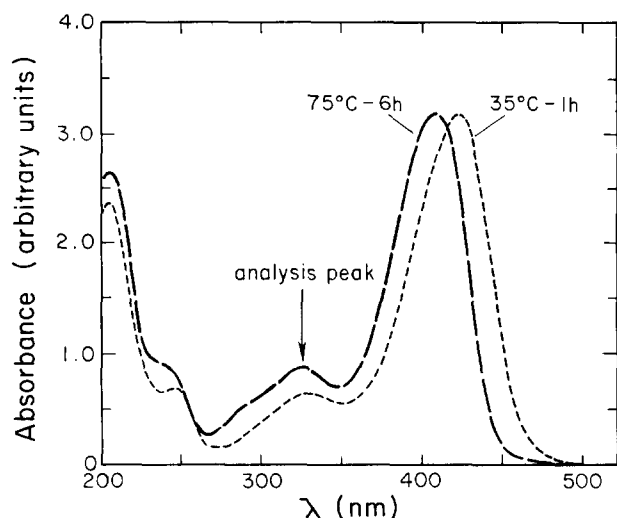


Figure 2 Absorbance spectra of partially sulfonated PEEK (35°C for ~ 1 h) and of completely sulfonated PEEK ($X = 1.0$, 75°C for 6 h) in 96.3% sulfuric acid

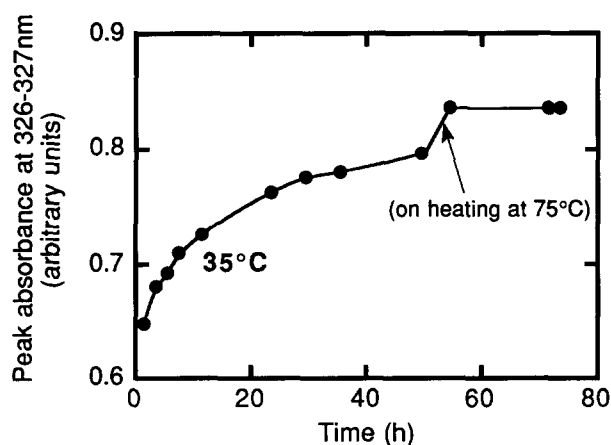


Figure 3 Kinetics of PEEK sulfonation in sulfuric acid: peak absorbance at 327 nm versus time

PEEK sulfonation progress is clearly reflected in the spectra, with gradually changing absorption intensities and band positions, as shown in Figure 2. The peak at 327 nm gradually grows as the reaction progresses and the growth shows that the band derived from the ketone group and that from the sulfonated A-ring overlap with each other. This growth may be attributed to the sulfonated A-ring since H_2SO_4 solutions of arylsulfonic acids have been reported to show their absorptions in the 250–340 nm region^{15–23}. The bands at around 245 and 280 nm increased, but the peak position and the absorbance change are both obscure, since they appeared as a shoulder on the neighbouring band. A blue shift occurred in the strong absorption at 420 nm to gradually move it to 408 nm during the reaction, without significant change of the intensity. This shift has been considered to have an insignificant effect on the absorbance of the 327 nm band from the shape and symmetry.

The band growth at 327 nm is considered to be suitable for kinetic measurement for the following reasons. The band position in wavelength was constant within a limit (326.9 ± 0.5 nm), and indicates that the band positions of the sulfonated A-ring and the diphenylketone group do not move during the sulfonation. The part of the peak height derived from the diphenylketone group is thought not to change since the number of the group is constant during the sulfonation. This part of the band is thus thought to be usable as the reference base level (I_0 , at $X = 0$) for the sulfonation measurement.

The growth of the 327 nm band was recorded as a time function at three constant sulfonation temperatures, 35, 55 and 75°C . The reaction proceeds much faster at higher temperature. The rate gradually slows with reaction time. For all the figures that follow, the origin of the timescale is set at the starting time of the mixing of PEEK powder with H_2SO_4 . The result at 35°C is given in Figure 3, as a typical example. Complete dissolution of the polymer took around 60, 30 and 15 min for the experiments at 35, 55 and 75°C , respectively.

Kinetic expressions with u.v.-vis. absorbance

The reference base level (I_0) is considered to be constant. The growth of the band height ($I - I_0$) in an absorbance mode at a time t is proportional to the concentration of sulfonated PEEK repeat unit ($C_0 - C$), according to equation (2)¹³:

$$I - I_0 = \epsilon(C_0 - C)b \quad (3)$$

At the end of the reaction, the concentration of the unsulfonated PEEK repeat unit (C) is zero. The difference of the band height between the beginning and the end of the reaction ($I_\infty - I_0$) is described as:

$$I_\infty - I_0 = \epsilon C_0 b \quad (4)$$

The fractional sulfonation, X , is the ratio of the concentrations of sulfonated PEEK repeat unit at a time, $t(C_0 - C)$, to that at the end of the reaction (C_∞), which equals the initial concentration of PEEK repeat unit (C_0). X may thus be described as a function of the u.v.-vis. absorbances and also as a function of the concentrations of the unsulfonated PEEK repeat unit:

$$X = \frac{I - I_0}{I_\infty - I_0} = \frac{C_0 - C}{C_0} \quad (5)$$

where C_0 and C represent the concentration of the

unsulfonated PEEK repeat unit at the beginning of the reaction ($t=0$) and that at a time t , $X=0$ at the beginning of the reaction and $X=1$ at the end ($t=\infty$) of the reaction. Equation (5) has been used to describe the relationship between the u.v.-vis. data and the kinetic equations.

The arylsulfonation rate in H_2SO_4 has been reported to be first order with respect to the aromatic ring concentration, second order in terms of H_2SO_4 concentration and inversely first order for water content^{7,8}. The second order of H_2SO_4 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. The effect of water on the reaction species has been considered to result in reaction retardation and thus appear as an inverse term^{7,8}. These terms may be treated as constant over a narrow range of H_2SO_4 concentration. In the experiment at an initial PEEK concentration of 0.023 g l^{-1} , the molar equivalent of water produced by complete sulfonation is $1.4 \times 10^{-3} \text{ g l}^{-1}$. This is negligible compared to the initial water (67.7 g l^{-1}) and insufficient to change the H_2SO_4 concentration on reaction.

If the sulfonation rate is simply first order with respect to the PEEK repeat unit concentration (C), the rate expression is:

$$-\frac{dC}{dt} = k_1 C \quad (6)$$

where t and k_1 represent the reaction time and the rate constant, respectively. This equation is integrated from the beginning of the reaction ($C=C_0$ at $t=0$) to a concentration (C at $t=t$) to give:

$$-\int_{C_0}^C \frac{dC}{C} = k_1 \int_0^t dt \quad (7a)$$

$$-\ln \frac{C}{C_0} = k_1 t \quad (7b)$$

Equation (7b) converts to equation (7c), the function of u.v.-vis. absorbances, using equation (5):

$$-\ln \frac{C}{C_0} = -\ln(1-X) = -\ln \frac{I_\infty - I}{I_\infty - I_0} = k_1 t \quad (7c)$$

If the rate is first order with respect to the substrate concentration, a plot of the logarithmic function of u.v.-vis. absorbances in equation (7c) versus time will follow a straight line with an appropriately selected I_0 . The least-squares fit of the plot will intersect (0,0). Curvature in Figure 4 shows that the reaction rate is not simply first order. No choice of I_0 makes the plots fit a straight line. Data simulate a linear function of time only in the early stage of the reaction, which is the so-called pseudo-first-order rate region. The rate becomes progressively slower than the pseudo-first-order rate.

We have reported that the rate of PEEK sulfonation is first order with respect to the unsulfonated PEEK repeat unit and inversely first order with respect to the concentration of the sulfonated PEEK repeat unit^{5,6}. This signifies that the reaction is retarded by the product, and has been explained by a sulfonation-desulfonation competing reaction, i.e. reversibility. If the product retardation exists in highly dilute condition, such as 0.02 g l^{-1} , the rate equation is described as:

$$-\frac{dC}{dt} = \frac{k_1 C}{k_d(C_0 - C)} \quad (8)$$

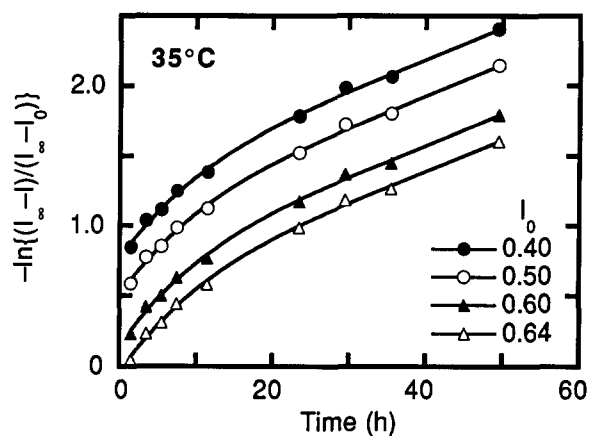


Figure 4 Kinetics of PEEK sulfonation in sulfuric acid: a typical example of the first-order treatment of u.v.-vis. spectroscopic data at 35°C

where k_d represents the rate constant of the inhibition or reverse reaction. Equation (8) is integrated from C_0 to C to give:

$$-\int_{C_0}^C \frac{C_0 - C}{C} dC = \frac{k_1}{k_d} \int_0^t dt \quad (9a)$$

$$-\frac{C_0 - C}{C_0} - \ln \frac{C}{C_0} = \frac{k_1}{k_d} \frac{1}{C_0} t \quad (9b)$$

Equation (9b) converts to equation (9c), the function of u.v.-vis. absorbances, using equation (5):

$$-X - \ln(1-X) = -\frac{I - I_0}{I_\infty - I_0} - \ln \frac{I_\infty - I}{I_\infty - I_0} = \frac{1}{C_0} \frac{k_1}{k_d} t \quad (9c)$$

If the rate is described as equation (8), a plot of the function of u.v.-vis. absorbances in equation (9c) versus time will fit a straight line with an appropriate value of I_0 . The proper I_0 will also make the least-squares fit of the plot intersect (0,0) and maximize the correlation coefficient, close to one. The value of I_∞ can be measured by a very long reaction time or by accelerating the reaction by raising the reaction temperature.

Extrapolation of I_0 and data treatment

The limit of I_0 is from zero to the absorbance of samples from the earliest stages of sulfonation. To find out the appropriate I_0 , one can select a candidate within the limits and put it into equation (9c) for trial calculations and plots. The least-squares fit of the plots gives the zero intercept and the correlation coefficient. These values are the means to evaluate the I_0 candidate. Several trials may be required to find out the most appropriate I_0 .

The results of the data calculations and the plots for the 35°C experiment are given in Figure 5, as a typical example of the procedure. In Figure 5, the zero intercept of the least-squares fit of the plot changes from positive to negative between values of 0.50 and 0.60 for I_0 . This indicates that the most appropriate I_0 exists between these values, and that the next candidates are to be selected from within their limit. Several repetitions of this trial give the results in Figure 6, in which the least-squares fit of the plot intersects (0,0) within the limit of significant figures, and the correlation coefficient has been maximized at $I_0=0.5992$. The data points fall on a

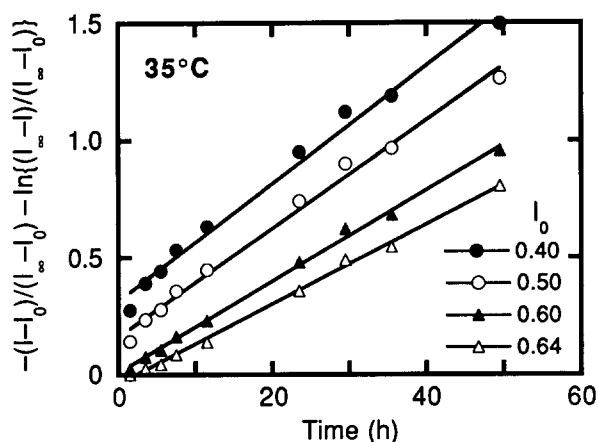


Figure 5 Kinetics of PEEK sulfonation in sulfuric acid at 35°C: a typical example of the data treatment with equation (9c). These are results of the first trial to extrapolate to I_0

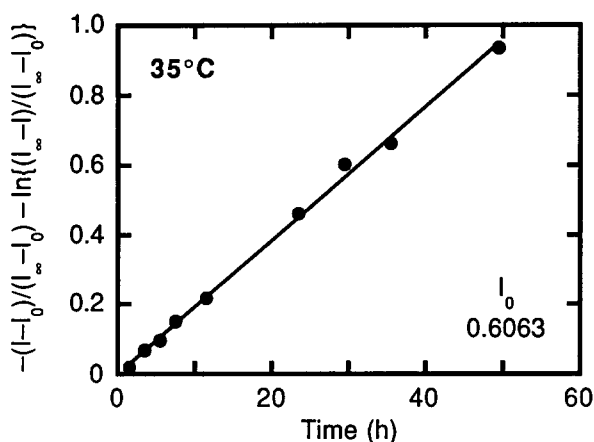


Figure 6 Kinetics of PEEK sulfonation in sulfuric acid at 35°C: typical results of the extrapolation of I_0 using the kinetic data treatment with equation (9c)

straight line. This confirms that the reaction rate is better described by equation (8), and is distinctly affected by a deflator derived from the reaction product. This result is consistent with our former report^{5,6} on sulfonation at relatively high PEEK concentration.

The result of the data treatment, shown in Figure 7, indicates that the data points follow a straight line at each temperature (35–75°C). The rate constant ratio (k_1/k_d) was obtained from the slope of the least-squares fits to these plots. Moreover, the fractional sulfonation, X , can be calculated using the relationship in equation (5) with the computed value of I_0 . The plot of X versus time shows how the sulfonation progresses and allows comparison with result at more concentrated conditions. The results are given in Figure 8. This figure shows that good agreement has been obtained between the reaction progress at 0.02 g l⁻¹ and that at 20.0 g l⁻¹ (refs 5, 6) over the temperature range of study.

An Arrhenius plot of the rate constant ratio (k_1/k_d) is given in Figure 9, which shows that the reaction follows the form of the Arrhenius equation over the temperature range of study (35–75°C). An activation energy (E_a) of 82.8 kJ mol⁻¹ repeating unit was calculated from the slope obtained from a least-squares fit. This value and the result (85.4 kJ mol⁻¹) at 20.0 g l⁻¹ (refs 5, 6) are in good agreement.

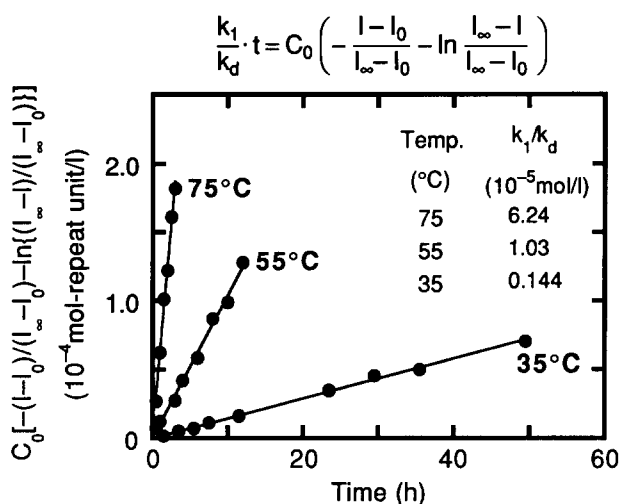


Figure 7 Kinetics of PEEK sulfonation in sulfuric acid: results of the data treatment with equation (9c) at 35, 55 and 75°C

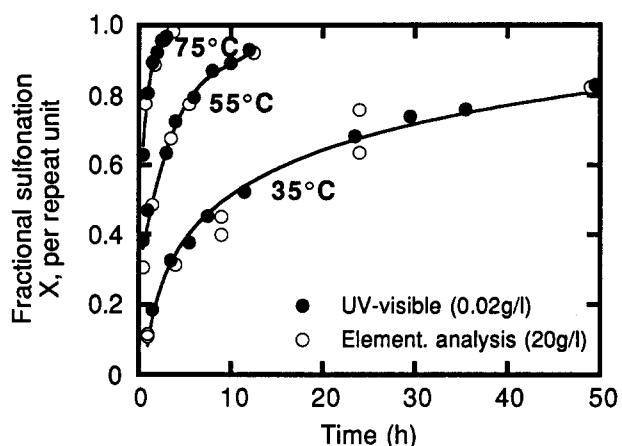


Figure 8 Kinetics of PEEK sulfonation in sulfuric acid at 35°C: comparison of the reaction progress at 0.02 and 20 g l⁻¹. X represents the fractional sulfonation per repeat unit

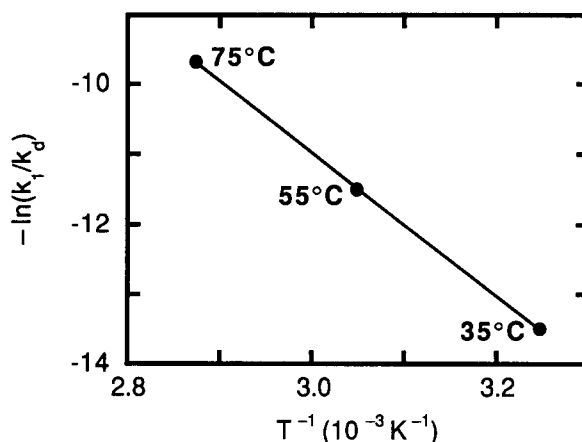


Figure 9 Arrhenius plot of the rate constant ratio (k_1/k_d). $\ln(k_1/k_d) = -9.97/T + 18.9$; correlation coefficient (R) = 0.99973; $E_a = 82.8$ kJ mol⁻¹ repeat unit

SUMMARY

The sulfonation kinetics of PEEK in 96.3% H₂SO₄ has been studied at highly dilute conditions (0.02 g l⁻¹) using the sensitive technique of u.v.-vis. spectroscopy. A lack of unsulfonated PEEK absorbance in the appropriate

range has been overcome by extrapolation using a statistical data treatment combined with the kinetic equation. The reaction rate is confirmed to be first order with respect to the concentration of unsulfonated PEEK repeat unit and inversely first order with respect to that of the sulfonated PEEK repeat unit. This result is explained by the coexistence of a competing reverse reaction, desulfonation. The sulfonation reaction follows the form of an Arrhenius equation over the temperature range of study (35–75°C), giving a calculated E_a of 82.8 kJ mol⁻¹ PEEK repeat unit. These new data and interpretations are consistent with our earlier results on PEEK reaction kinetics at higher concentration (20 g l⁻¹).

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