

# Sulfonation Reaction Kinetics of Poly(ether ketone ketone) (PEKK) Using a Mixture of Concentrated and Fuming Sulfuric Acid

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Sulfonated poly(ether ketone ketone) (SPEKK) ionomers were prepared by sulfonating PEKK with a mixture of concentrated and fuming sulfuric acid. Sulfonation occurs only on the phenyl rings attached to ether and ketone groups, resulting in a maximum sulfonation level of 4.33 mequiv/g. Three models for the reaction kinetics were investigated: (i) a second-order model and (ii) a pseudo-first-order model, each based on a single reaction step between active PEKK sites and  $\text{SO}_3$ , and (iii) a consecutive-reactions approach based on the notion that a previously reacted PEKK site deactivates remaining sites in the same repeat unit. Activation energies ranging from 71 to 76 kJ/mol were found for reaction temperatures from 16 to 74 °C. Although the sulfonation reaction could be predicted adequately up to a sulfonation level of 2.5 mequiv/g with all proposed models, the third model was needed to extend the simulation capability beyond this point. The validity of the consecutive-reactions model was confirmed by investigating the effect of the terephthaloyl-to-isophthaloyl ratio in PEKK and the effect of the initial  $\text{SO}_3$  concentration.

## Introduction

Poly(aryl ether ketone)s, PAEEKs, are aromatic polymers with excellent thermal stability, chemical resistance, and mechanical properties. These high-temperature thermoplastics can be obtained with different ratios of arylene ether and arylene ketone groups. Apart from the most commonly used poly(ether ether ketone), PEEK, other commercial PAEEKs are poly(ether ketone), PEK, and poly(ether ketone ketone), PEKK.

Sulfonated PEEK (SPEEK) is of great interest as solution-cast membranes offer proton conductivities that compete with those of perfluorosulfonate ionomer membranes such as Nafion.<sup>1–3</sup> Promising performance data have been reported for both hydrogen/oxygen fuel cells<sup>4</sup> and direct methanol fuel cells.<sup>5</sup> SPEEK has been used as a component in polymer blends aiming at high-temperature fuel cell performance without compromising mechanical stability.<sup>6–8</sup> In this work, the sulfonation reaction mechanism and kinetics of PEKK are studied. The thermal properties, water uptake, and performance of SPEKK as a proton-exchange membrane (PEM) material are discussed elsewhere.<sup>9</sup> One of the reasons to select PAEEKs with a higher K/E ratio is the concomitant increase in oxidative stability.<sup>10</sup> Moreover, the fuel cell requirements of PEMs based on SPAEEKs have to be kept in mind: high proton conductivities should be combined with limited swelling in an aqueous environment. In this respect, higher K/E ratios allow for higher permissible sulfonation levels,<sup>11</sup> resulting in increased proton conductivities.<sup>9</sup>

The mechanism and kinetics of the electrophilic sulfonation reaction have been studied extensively for small aromatics as summarized in Cerfontain.<sup>12</sup> With concentrated sulfuric acid as the sulfonating agent, the reaction rate was found to be first order in the aromatic ring concentration and second order in concentrated

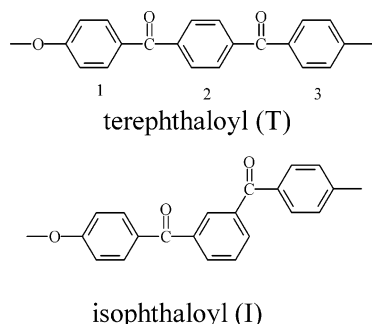
sulfuric acid. Water, formed as a byproduct, retards the reaction. A combination of these reaction steps has led to the following expression for the consumption rate of active aromatic hydrogen sites<sup>12</sup>

$$-\frac{d[\text{Ar-H}]}{dt} = \frac{k[\text{Ar-H}][\text{H}_2\text{SO}_4]^2}{[\text{H}_2\text{O}]} \quad (1)$$

where  $[\text{Ar-H}]$ ,  $[\text{H}_2\text{SO}_4]$ , and  $[\text{H}_2\text{O}]$  are the concentrations of the aromatic ring, sulfuric acid, and water, respectively, and  $k$  is the rate constant. Sulfuric acid acts as a sulfonating agent and assists in proton removal from the aromatic ring,<sup>12</sup> hence the second-order dependence in eq 1.

A few research groups have studied the sulfonation of PEEK with concentrated sulfuric acid. The aromatic ring attached to electron-donating groups such as the two ether groups in the oxy-phenylene-oxy units can be sulfonated under these conditions, resulting in a maximum of one sulfonic acid group per repeat unit, while free sulfur trioxide is needed to sulfonate the ring in the oxy-phenylene-carbonyl units.<sup>11</sup> In conditions where a large excess of concentrated sulfuric acid and a low initial water concentration are used, the concentrations of these components can be considered to be constant in eq 1, resulting in a pseudo-first-order model in  $\text{Ar-H}$ . This was reported by Huang et al.<sup>13</sup> for the sulfonation of PEEK. Daoust et al.<sup>14–16</sup> noticed a deviation from the first-order kinetics, which they attributed to a long-range deactivation effect of the electron-withdrawing sulfonate groups. To incorporate this effect in the reaction mechanism, unsulfonated, monosulfonated, and disulfonated dimers were defined as separate species and combined in consecutive first-order reaction steps. On the other hand, Shibuya and Porter<sup>17–19</sup> reported that the reaction is first order in the concentration of the PEEK chain repeat unit and inversely proportional to the concentration of sulfonated PEEK units. The latter effect was attributed to a

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**Figure 1.** Chemical structure of the repeat unit of poly(ether ketone ketone) (PEKK).

competing desulfonation reaction that occurs for aryl-sulfonic acids in acidic media.

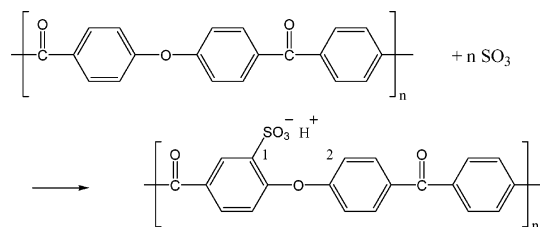
PEKK is a family of copolymers with different ratios of terephthaloyl (T) and isophthaloyl (I) moieties (Figure 1). As indicated before, sulfonation of PEKK requires strong sulfonation reagents, because the ketone groups withdraw electron density from the aromatic ring. Ulrich and Rafler<sup>11</sup> reported sulfonating PEKK using mixtures of sulfuric acid and fuming sulfuric acid (gaseous SO<sub>3</sub> dissolved in H<sub>2</sub>SO<sub>4</sub>). Bauer et al.<sup>20,21</sup> also described the sulfonation of PEKEKK, which has a slightly lower K/E ratio than PEKK, with sulfuric acid and fuming sulfuric acid, as well as the sulfonations of PEEKK and PEEK and their use as ion-exchange membranes. Soczka-Guth et al.<sup>22</sup> reported the use of sulfonated PEK membranes in fuel cells. No systematic study has, however, been conducted on the reaction kinetics of sulfonation in the presence of this strong sulfonating agent.

## Experimental Section

**Materials.** PEKK samples with T/I ratios of 8/2 [OXPEKK-C,  $T_g = 164$  °C,  $T_M = 360$  °C,  $M_w = 137000$  g/mol,  $M_n = 27000$  g/mol,  $\eta(T = T_M + 20$  °C) = 1000 Pa·s] and 6/4 [OXPEKK SPb,  $T_g = 154$  °C,  $T_M = 300$  °C,  $\eta(T = T_M + 20$  °C) = 6000 Pa·s] were obtained from Oxford Performance Materials, Enfield, CT. No molecular weight data were available for OXPEKK SPb. A comparison of the melt viscosities of the two polymers, however, indicates that the 6/4 copolymer has a higher molecular weight.

Concentrated sulfuric acid (96.3% H<sub>2</sub>SO<sub>4</sub>,  $\rho = 1.84$  g/mL) and fuming sulfuric acid (26% free SO<sub>3</sub>,  $\rho = 1.925$  g/mL) were obtained from Fisher Scientific. The amounts of water in concentrated sulfuric acid and of SO<sub>3</sub> in fuming sulfuric acid were checked by titration. Mixing concentrated sulfuric acid with fuming sulfuric acid in a 53/47 (v/v) ratio, for example, corresponds to an initial SO<sub>3</sub> concentration of 0.7 mol/L.

To study the reaction progress at different reaction times, aliquots were extracted by opening the reaction environment to air for short periods of time. The amount of water introduced into the reaction vessel in this way can be calculated from a psychrometric chart, assuming, for example, a relative humidity of 60% at 25 °C: 0.012 kg of H<sub>2</sub>O/kg of air. The volume of the reaction vessel was 500 mL, of which 100 mL was initially occupied by the reaction mixture. If one assumes that the H<sub>2</sub>O in the added air dissolves in the acidic medium, the concentration of H<sub>2</sub>O introduced into the reactive mixture increases from 0.004 to 0.03 mol/L during 10 sequential extractions of 10 mL each.



**Figure 2.** Basic reaction scheme during sulfonation of a PEKK repeat unit with the SO<sub>3</sub> from fuming sulfuric acid.

**Sulfonation Conditions.** Sulfonation of PEKK (5% w/v) was typically performed in a mixture of 53/47 (v/v) concentrated sulfuric acid and fuming sulfuric acid. To ensure homogeneous sulfonation conditions, PEKK was first dissolved in sulfuric acid, in which no reaction occurs. Subsequently, fuming sulfuric acid was added, and this time was taken as zero reaction time. Note that PEKK with a T/I ratio of 6/4 takes about 6 h to dissolve in sulfuric acid, whereas PEKK with a T/I ratio of 8/2 takes only 30 min, again indicating the higher molecular weight of the former. Sulfonation temperatures ranged from 15 to 80 °C.

The resulting sulfonated polymer, SPEKK, was precipitated by dropwise addition of the solution into six volumes of rapidly stirred deionized ice water. The SPEKK was filtered, washed repeatedly with deionized water to remove excess acid, and dried at 60 °C overnight and then under vacuum at 120 °C for 3 days. The sulfonation level is expressed as an ion-exchange capacity (IEC), defined as the concentration of sulfonate groups in equivalents per unit mass. Because SPEKK with an IEC higher than 2.4 mequiv/g is soluble in water, a cellulose dialysis membrane (Fisher Scientific) was used to extract residual free sulfuric acid. Note that a highly sulfonated SPEKK sample still precipitates in deionized ice water in the presence of sulfuric acid.

The sulfonation level was determined by titration of the sulfonic acid groups. SPEKK was ion-exchanged with an excess saturated aqueous sodium chloride solution overnight. The hydrogen chloride product was then titrated with a normalized sodium hydroxide solution using phenolphthalein as an acid–base indicator. The IEC obtained in this way agreed very well with values obtained from elemental analysis.<sup>9</sup> To further confirm the sulfonation level and ensure that no sulfuric acid remained in the washed SPEKK, thermogravimetric analysis was performed on all samples.<sup>9</sup>

## Results and Discussion

**Reaction Mechanism. Equal Reactivity of Active Sites in PEKK.** A schematic representation of the reaction between PEKK and free SO<sub>3</sub> is depicted in Figure 2. Both positions 1 and 2 can be sulfonated once, in theory leading to a maximum sulfonation level ( $X_s$ ) of 2, as confirmed from <sup>13</sup>C NMR spectroscopy.<sup>11</sup> Note that the phenylene ring in the carbonyl–phenylene–carbonyl unit cannot be sulfonated.<sup>11</sup> To compare different ionomers, the ion-exchange capacity (IEC), defined as the number of moles of sulfonate groups per gram of polymer, is more useful

$$\text{IEC (mequiv/g)} = 1000 \frac{X_s}{300 + 81X_s} \quad (2)$$

Equation 2 results in a maximum IEC of 4.33 mequiv/g.

In contrast to sulfonation with concentrated sulfuric acid (see eq 1), no additional water is formed during sulfonation with free  $\text{SO}_3$ .<sup>12</sup> A simple, second-order reaction mechanism (Scheme 1) can therefore be considered:

**Scheme 1. Reaction of Active Sites in the Repeat Unit of PEKK<sup>a</sup> with  $\text{SO}_3$ , Leading to a Partially Sulfonated SPEKK<sup>b</sup>**



<sup>a</sup>Ar-H, see Figure 2, positions 1 or 2. <sup>b</sup> $k_S$  = reaction rate constant.

The consumption rate of Ar-H can be obtained from inspection of Scheme 1

$$-\frac{d[\text{Ar-H}]}{dt} = k_S[\text{Ar-H}][\text{SO}_3] \quad (3)$$

where [Ar-H] and  $[\text{SO}_3]$  are the concentrations of active aromatic sites and free  $\text{SO}_3$ , respectively, in moles per liter and  $k_S$  is the sulfonation reaction rate constant in liters per mole per second.

By integration of eq 3, using the mass balance of Scheme 1 and setting  $P = [\text{Ar-H}]$ ,  $S = [\text{SO}_3]$ , and  $P_S = [\text{Ar-SO}_3\text{H}]$  (subscript 0 denotes concentrations at time zero), the following relation can be found for the concentration of sulfonated phenylene groups formed (see Appendix)

$$P_S = \frac{P_0 S_0 (1 - e^{-k_S t (S_0 - P_0)})}{S_0 - P_0 e^{-k_S t (S_0 - P_0)}} \quad (4)$$

For the case of excess  $\text{SO}_3$ , a pseudo-first-order kinetic equation is obtained

$$-\frac{dP}{dt} = k'_S P \quad (5)$$

where  $k'_S = k_S S_0$  and  $S_0$  is the concentration of  $\text{SO}_3$  at time  $t = 0$ .

This results in the following equation for  $P_S$

$$P_S = P_0 (1 - e^{-k'_S t}) \quad (6)$$

An Arrhenius relation was used for the reaction rate constant

$$\ln k_S = \ln A_S - \frac{E_S}{RT} \quad (7)$$

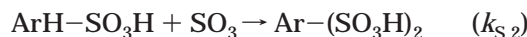
Note that the IEC (mequiv/g) of SPEKK can be obtained from  $P_S$  via

$$\text{IEC} = P_S / C \quad (8)$$

with  $C$  (g/mL) as the concentration of polymer in the sulfuric acid/fuming sulfuric acid mixture.

**Consecutive-Reactions Approach.** The conversion of one active phenylene site in the repeat unit of PEKK (position 1 or 2 in Figure 2) to an electron-withdrawing sulfonate group might deactivate the conversion of the second active site. A simple scheme of consecutive reactions can be used to incorporate this effect.

**Scheme 2. Consecutive Reaction of a PEKK Repeat Unit with Two Active Phenylene Sites ( $\text{Ar-H}_2$ ) Followed by the Reaction of an Active Phenylene Site in a Repeat Unit with One Reacted Site ( $\text{ArH-SO}_3\text{H}$ ), Resulting in a Fully Sulfonated Repeat Unit  $[\text{Ar-(SO}_3\text{H)}_2]$**



A similar approach, though on a longer range between neighboring repeat units, was proposed for sulfonation of PEEK with concentrated sulfuric acid.<sup>14-16</sup> The closer proximity of the active reaction sites in the case of PEKK calls for the introduction of Scheme 2.

If one assumes a pseudo-first-order rate for both reactions and sets  $P_{S,1} = [\text{ArH-SO}_3\text{H}]$ ,  $P_{S,2} = [\text{Ar-(SO}_3\text{H)}_2]$ , and  $P = [\text{Ar-H}_2]$ , the following relation is obtained for the time-resolved IEC (see the Appendix)

$$\begin{aligned} \text{IEC} &= (P_{S,1} + P_{S,2}) / C \\ &= \frac{P_0}{C} \left( 1 - \frac{k_{S,2} - k_{S,1}}{k'_{S,2} - 2k'_{S,1}} e^{-2k'_{S,1}t} + \frac{k_{S,1}}{k'_{S,2} - 2k'_{S,1}} e^{-k'_{S,2}t} \right) \end{aligned} \quad (9)$$

**Optimization Strategy.** The kinetic rate constants of the three models, namely, (i) pseudo-first-order in Ar-H (eqs 6 and 8), (ii) first-order in Ar-H and  $\text{SO}_3$  (eqs 4 and 8), designated as the second-order model, and (iii) consecutive-reactions approach (eq 9), were determined by a curve-fitting procedure. All sulfonation temperatures were optimized simultaneously in a least-sum-of-squares procedure. In this way, one set of preexponential factors ( $A$ ) and activation energies ( $E$ ) can be obtained for the three models (see Tables 1 and 2 for PEKK 8/2 and PEKK 6/4, respectively). The initial concentration of free  $\text{SO}_3$  was 0.7 mol/L for a ratio of concentrated sulfuric acid to fuming sulfuric acid (v/v) of 53/47 (see the Experimental Section). The IEC reached after infinite time,  $\text{IEC}_\infty$ , was 4.33 mequiv/g, corresponding to two sulfonated groups per repeat unit (eq 2).

**Model Optimization. Effect of Sulfonation Temperature.** The effect of reaction temperature on the time evolution of the IEC is shown in Figure 3 for PEKK with a T/I ratio of 8/2. All three reaction models depict the effect of reaction temperature on overall reaction rate adequately. An activation energy of around 75 kJ/mol was obtained (see Table 1). This corresponds reasonably well to values obtained for the sulfonation of PEEK in concentrated sulfuric acid (range reported in the literature:<sup>13,17,19</sup> 79–85 kJ/mol). Note that open symbols in Figure 3 correspond to one reaction mixture from which subsequent aliquots were extracted for analysis (designated “open”). Closed symbols correspond to separate, independent reaction mixtures. The possible difference between these two approaches will be explored later.

The pseudo-first-order and second-order reaction model simulations deviate significantly from the experimental trend for long sulfonation times (notice sulfonation temperatures 40 and 52 °C). The former model assumes that the  $\text{SO}_3$  concentration is constant and equal to the initial concentration, whereas the latter allows this



**Table 1. Kinetic Parameters for the Three Sulfonation Reaction Models as Obtained from a Least-Sum-of-Squares Optimization for PEKK with a T/I ratio of 8/2**

model	$E_S$ , kJ/mol	$k_S$ at 52 °C, $10^{-5}$ L/(mol·s)
pseudo-first-order (eqs 5 and 8)	$76 \pm 4$	$1.57 \pm 0.08$
second-order (eqs 4 and 8)	$75 \pm 4$	$1.8 \pm 0.1$
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	$E_{S,1}$ , kJ/mol	$k_{S,1}$ at 52 °C, $10^{-5}$ L/(mol·s)
consecutive pseudo-first-order (eq 9)	$75 \pm 3$	$2.6 \pm 0.1$
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	$E_{S,2}$ , kJ/mol	$k_{S,2}$ at 52 °C, $10^{-5}$ L/(mol·s)
consecutive pseudo-first-order (eq 9)	$80 \pm 14$	$0.33 \pm 0.04$

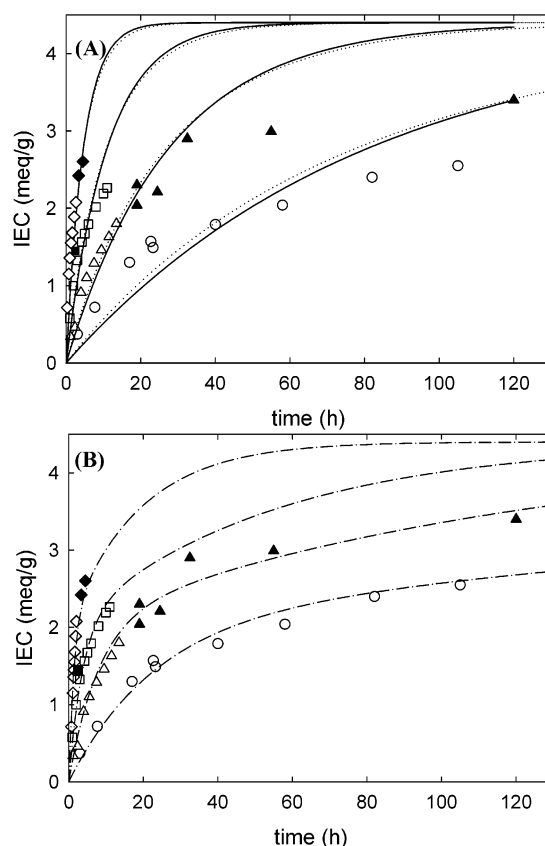
**Table 2. Kinetic Parameters as Obtained from a Least-Sum-of-Squares Optimization for PEKK (T/I ratio 6/4)**

model	$E_S$ , kJ/mol	$k_S$ at 52 °C, $10^{-5}$ L/(mol·s)
pseudo-first-order (eqs 5 and 8)	$71 \pm 4$	$4.1 \pm 0.3$
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	$E_{S,1}$ , kJ/mol	$k_{S,1}$ at 52 °C, $10^{-5}$ L/(mol·s)
consecutive pseudo-first-order (eq 9)	$72 \pm 5$	$7.6 \pm 0.9$
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	$E_{S,2}$ , kJ/mol	$k_{S,2}$ at 52 °C, $10^{-5}$ L/(mol·s)
consecutive pseudo-first-order (eq 9)	$80 \pm 280$	$0.1 \pm 0.3$

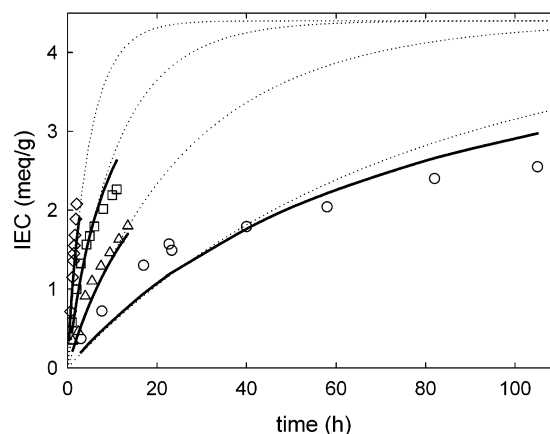
concentration to change during the reaction. The small difference in reaction advancement between the two simulations results from the fact that  $\text{SO}_3$  is in excess in the conditions of Figure 3A. This detail will be clarified later by simulating the effect of the initial  $\text{SO}_3$  concentration.

A better fit is obtained in Figure 3B by using the consecutive-reactions approach, indicating that the retardation effect probably becomes important at later stages of the reaction. As can be concluded from Table 1, the reaction rate constant for the addition of the second sulfonate group in the same repeat unit ( $k_{S,2}$  in Scheme 2) is an order of magnitude lower than  $k_{S,1}$ . Longer-than-expected reaction times are thus needed to sulfonate PEKK beyond an IEC of 2.5 mequiv/g. The difference in reaction rate also means that sulfonate groups are not distributed randomly among repeat units in partially sulfonated SPEKK. Concretely, simulation with the parameters of Table 1 finds that, after 50% sulfonation, 91% of the repeat units have only one sulfonate per repeat unit. This information might be important for understanding the performance of SPEKK-based PEMs given that proton conductivity depends in part on the distance between the acidic sites.<sup>23</sup>

A concern might be raised about the introduction of water into the reaction environment when aliquots were extracted at different sulfonation times (open symbols in Figure 3). This could result in an apparent retardation effect, which therefore has to be excluded to ensure the validity of the consecutive-reactions model. Although care was taken to reduce the exposure time of the mixture during the extractions (less than 1 min), small amounts of water, resulting in a depletion of the available  $\text{SO}_3$  groups, might have a considerable retardation effect. As was estimated in the Experimental Section, additional water introduced in this way corresponds to concentrations ranging from 0.004 to 0.03 mol/L during subsequent extractions. As an example,

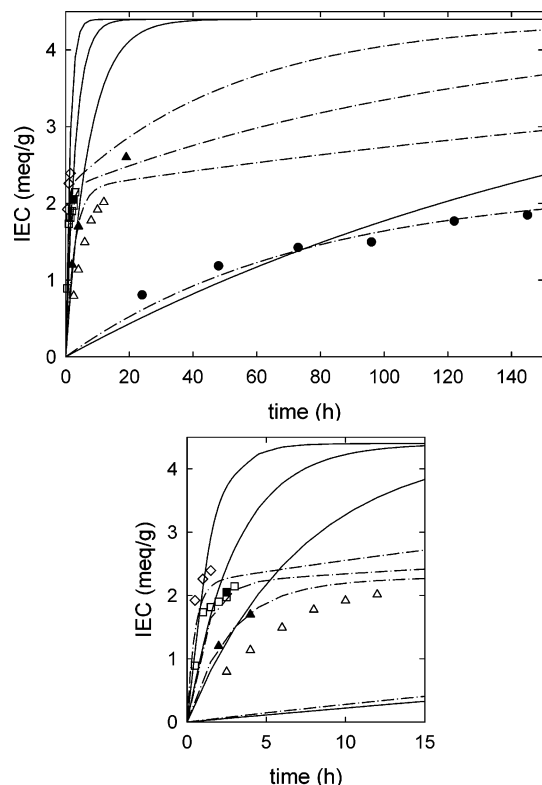


**Figure 3.** Evolution of the IEC with time for PEKK (T/I ratio = 8/2) in a 53/47 (v/v) concentrated sulfuric acid/fuming sulfuric acid mixture at different reaction temperatures: 40 °C (○), 52 °C (open, △; closed, ▲), 63 °C (open, □; closed, ■), 74 °C (open, ◇; closed, ◆); (A) simulation using the optimized set of kinetic parameters (Table 1) for the pseudo-first-order model (eqs 6 and 8, solid line) and the second-order model (eqs 4 and 8, dotted line); (B) simulation of the consecutive reaction approach (eq 9, dash-dot line).



**Figure 4.** Simulation with the second-order model (thick solid line) of the effect of water additions on the evolution of the IEC with time for PEKK (T/I ratio 8/2) in a 53/47 (v/v) concentrated sulfuric acid/fuming sulfuric acid mixture; experimental points (symbols); assumption,  $[\text{H}_2\text{O}] = 0.02$  mol/L (see text) added with each sample extraction; 40 °C (○), 52 °C (△), 63 °C (□), 74 °C (◇); simulation without water additions (dotted line).

the effect of adding 0.02 mol/L water for each experimental point in time is simulated in Figure 4. To include the effect of a changing intermittent  $\text{SO}_3$  concentration, the second-order model was the most appropriate. Note that the consecutive-reactions approach is not needed here because the experimental data were restricted to IECs below 2.5 mequiv/g. The simulation was performed



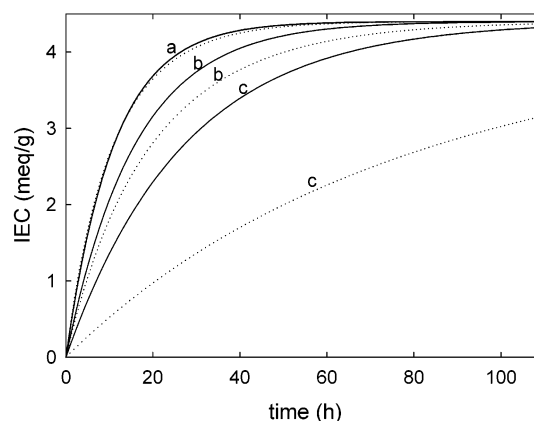
**Figure 5.** Evolution of the IEC with time for PEKK (T/I ratio 6/4) in a 53/47 (v/v) concentrated sulfuric acid/fuming sulfuric acid mixture at different reaction temperatures: 16 °C (closed, ●), 52 °C (open, △; closed, ▲), 63 °C (open, □; closed, ■), 74 °C (open, ◇); simulation using the optimized set of kinetic parameters (Table 2) for the pseudo-first-order model (eqs 6 and 8, solid line); simulation of the consecutive-reactions approach (eq 9, dash-dot line). The bottom graph shows an enlargement of the low sulfonation times.

with the second-order model (Table 1) by resetting the initial  $\text{SO}_3$  concentrations at each extraction time (corresponds to symbols in Figure 4). Only the lowest sulfonation temperature shows a significant deviation between the simulations. Deviations between experiment and simulation in Figure 3 are therefore not likely to be caused by the introduction of water.

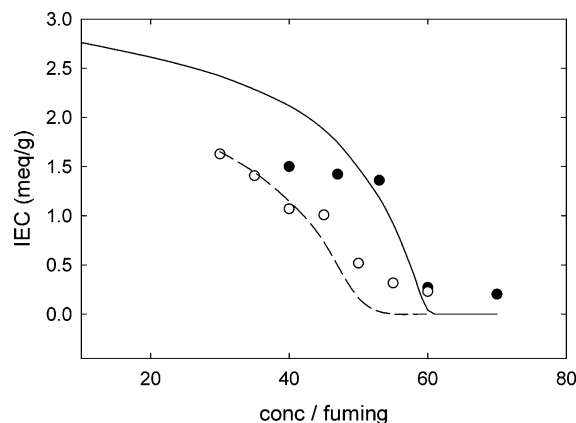
**Effect of the T/I Ratio.** Figure 5 shows the results of the fitting procedure for the sulfonation of PEKK with a T/I ratio of 6/4. Larger deviations between simulation and experiment are seen here. This result can tentatively be attributed to the much slower dissolution of the higher-molecular-weight polymer in concentrated sulfuric acid. Reaction time zero, defined as the time at which fuming sulfuric acid was added, might therefore be less accurate.

As was the case for PEKK with a T/I ratio of 8/2, the consecutive-reactions approach resulted in a better fit. Also note that the sulfonation rate of PEKK with a T/I ratio of 6/4 was about 3 times higher than that of the 8/2 isomer (compare the kinetic parameters in Tables 1 and 2). This effect is difficult to explain in view of the higher molecular weight of the former isomer. It might be related to the higher flexibility of the 6/4 chain.

**Effect of the Free  $\text{SO}_3$  Concentration.** The pseudo-first-order and second-order models (Figure 3A) almost coincide for a ratio of concentrated sulfuric acid to fuming sulfuric acid of 53/47 (v/v), mostly used in this work. This ratio results in an initial  $\text{SO}_3$  concentration of 0.7 mol/L. This corresponds to an excess in  $\text{SO}_3$  as 0.22 mol/L  $\text{SO}_3$  is required to attain the maximum IEC



**Figure 6.** Simulation of the effect of the concentrated sulfuric acid/fuming sulfuric acid ratio on the reaction at 63 °C of PEKK (T/I ratio 8/2): pseudo-first-order model (solid line) and second-order model (dotted line) at ratios (v/v) of (a) 53/47, (b) 55/45, and (c) 57/43, corresponding to initial  $\text{SO}_3$  concentrations of (a) 0.7, (b) 0.5, and (c) 0.3 mol/L.



**Figure 7.** IEC reached for sulfonation of PEKK 8/2 at 74 °C for 1 h (●, solid line, simulation) and PEKK 6/4 at 16 °C for 24 h (○, dashed line, simulation) using different initial  $\text{SO}_3$  contents; simulations were performed using the consecutive-reactions approach.

of 4.33 mequiv/g. When the ratio is increased, however, the initial concentration of  $\text{SO}_3$  drops significantly because of the dilution by concentrated sulfuric acid and, more importantly, because of the introduction of additional water (see also the Experimental Section). It is assumed here that, upon mixing, water will react immediately with free  $\text{SO}_3$  groups to form  $\text{H}_2\text{SO}_4$ , which is nonreactive toward active PEKK sites. Small changes in the ratio therefore result in large differences between the two models (simulated in Figure 6) as  $\text{SO}_3$  quickly ceases to be the excess component.

To illustrate the need for using free  $\text{SO}_3$  as a reactant for the sulfonation of PEKK, in contrast to the milder conditions for sulfonating PEEK, Figure 7 shows the effect of the initial volume ratio of concentrated to fuming sulfuric acid on the extent of sulfonation. Different conditions (sulfonation time and temperature) were selected for the two isomers to illustrate the flexibility of the reaction model. As indicated before, it is assumed that the additional water added by increasing the content of concentrated sulfuric acid was converted to  $\text{H}_2\text{SO}_4$  by the free  $\text{SO}_3$  groups immediately upon mixing.

The trend in sulfonation level is predicted by the consecutive-reactions approach using eq 9 and the optimized parameters of Tables 1 and 2. This model,

based on two pseudo-first-order reactions, is less reliable when  $\text{SO}_3$  is no longer in excess with respect to the active PEKK sites. From the discussion regarding Figure 6, ratios of concentrated to fuming sulfuric acid above 55/45 can therefore not be simulated with this approach.

## Conclusions

Sulfonated poly(ether ketone ketone) is a promising proton-conducting polymer for fuel cell applications. The sulfonation requires strong reagents, such as mixtures of concentrated and fuming sulfuric acid. A model for the reaction kinetics allows for accurate control of the sulfonation level. Only free  $\text{SO}_3$  is sufficiently reactive toward the active PEKK sites, resulting in sulfonic acid group formation. Models based on the assumption that all active sites in PEKK are of equal reactivity can describe the first 50% of sulfonation. When volumetric ratios of concentrated sulfuric acid to fuming sulfuric acid lower than 55/45 are used, a simple pseudo-first-order model can be used to describe the reaction in this region. For higher ratios, the  $\text{SO}_3$  groups cannot be assumed to be in excess because the initial  $\text{SO}_3$  concentration is significantly reduced by its reaction with the water present in concentrated sulfuric acid. In this case, a second-order model is needed. The validity of this model and its parameters has been checked by simulating the effect of the initial  $\text{SO}_3$  concentration.

Beyond the first 50% of reaction, a retardation effect becomes apparent that originates from the deactivation of the sulfonate groups neighboring the remaining active sites. The complete sulfonation reaction can be described by two consecutive reactions. The addition of the second sulfonate group in the same repeat unit is an order of magnitude slower than the addition of the first sulfonate group. This will affect the distribution of these groups along the polymer backbone for different sulfonation levels, which might be important for the application of SPEKK as a proton-exchange membrane material.

Decreasing the ratio of terephthaloyl (T) to isophthaloyl (I) in PEKK from 8/2 to 6/4 results in a 3-fold increase in sulfonation rate, which might be related to the higher flexibility of the 6/4 copolymer.

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## Appendix

**Second-Order Reaction Mechanism.** Applying the mass balance in Scheme 1, eq 3 can be written as

$$\frac{dP_S}{dt} = k_S(P_0 - P_S)(S_0 - P_S)$$

Rearranging gives

$$\frac{1}{S_0 - P_0} \left( \frac{dP_S}{P_0 - P_S} - \frac{dP_S}{S_0 - P_S} \right) = k_S dt$$

Integration from  $t = 0$  to  $t = t$  yields

$$\frac{1}{S_0 - P_0} \ln \left( \frac{P_0 S_0 - P_S}{S_0 P_0 - P_S} \right) = k_S t$$

or

$$\frac{S_0 - P_S}{P_0 - P_S} = \frac{S_0}{P_0} e^{k_S t (S_S - P_0)}$$

This expression can be rearranged to give an explicit equation for  $P_S$ , given in eq 4.

**Consecutive-Reactions Approach.** Inspection of Scheme 2 reveals the expressions

$$-\frac{dP}{dt} = 2k_{S,1}(P_0 - P_{S,1})S$$

$$\frac{dP_{S,2}}{dt} = k_{S,2}(P_{S,1} - P_{S,2})S$$

In the assumption that  $\text{SO}_3$  is present in excess, two consecutive pseudo-first-order reactions can be written

$$-\frac{dP}{dt} = 2k_{S,1}(P_0 - P_{S,1})S_0 = 2K'_{S,1}(P_0 - P_{S,1})$$

$$\frac{dP_{S,2}}{dt} = k_{S,2}(P_{S,1} - P_{S,2})S_0 = K'_{S,2}(P_{S,1} - P_{S,2})$$

where  $K'_{S,1} = k_{S,1}S_0$  and  $K'_{S,2} = k_{S,2}S_0$ .

Integrating the first rate equation and substituting into the second gives

$$P_{S,1} = P_0(1 - e^{-2K'_{S,1}t})$$

$$\frac{dP_{S,2}}{dt} + K'_{S,2}P_{S,2} = K'_{S,2}P_0(1 - e^{-2K'_{S,1}t})$$

The second equation can be integrated by substituting  $P_{S,2}$  for the sum of two exponential functions and solving for the introduced parameters, finally resulting in

$$P_{S,2} = P_0 \left( 1 - \frac{K'_{S,2}}{K'_{S,2} - 2K'_{S,1}} e^{-2K'_{S,1}t} + \frac{2K'_{S,1}}{K'_{S,2} - 2K'_{S,1}} e^{-K'_{S,2}t} \right)$$

Equation 9 can now be obtained from

$$\begin{aligned} P_{S,1} + P_{S,2} &= P_0 \left( 2 - \frac{K'_{S,2} - 2K'_{S,1}}{K'_{S,2} - 2K'_{S,1}} e^{-2K'_{S,1}t} - \frac{K'_{S,2}}{K'_{S,2} - 2K'_{S,1}} e^{-2K'_{S,1}t} + \frac{2K'_{S,1}}{K'_{S,2} - 2K'_{S,1}} e^{-K'_{S,2}t} \right) \\ &= 2P_0 \left( 1 - \frac{K'_{S,2} - K'_{S,1}}{K'_{S,2} - 2K'_{S,1}} e^{-2K'_{S,1}t} + \frac{K'_{S,1}}{K'_{S,2} - 2K'_{S,1}} e^{-K'_{S,2}t} \right) \end{aligned}$$

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