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Proton-Exchange Membranes by Radiation Grafting of Styrene onto FEP Films. II. Mechanism of Thermal Degradation in Copolymer Membranes

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SYNOPSIS

The thermal degradation of radiation-grafted and sulfonated FEP-g-polystyrene membrane has been investigated in the temperature range 50–650°C in an inert gas atmosphere by thermogravimetry. The evolved gaseous products were analyzed by FTIR in combination with mass spectrometry to correlate weight losses at different temperatures with molecular composition of the copolymer membrane. On the basis of these results, a simple degradation model has been established. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Preparation of permselective membranes by radiation grafting of hydrophilic monomers onto polymeric films is an attractive route due to its versatility in controlling the graft composition by careful variation of the dose and dose rate of radiation.[1-6] During such a process, the monomer is polymerized in the presence of a preformed polymer film so that the modified polymer acquires some additional properties of the grafted moiety. We have synthesized strong cation-exchange membranes by the simultaneous radiation grafting of styrene monomer onto FEP films, followed by their sulfonation.[6,7] The hydrophilic membranes, obtained by this two-step process, show a high degree of conductivity ($\sim$ 0.3 S $\times$ cm^{-1} at 20°C for 40% polystyrene content). Such membranes have generated considerable interest in fuel cell, electrolyzer, and other electrochemical applications.[7-12] The performance of such systems largely depends upon the nature and stability of the membrane used for a particular application.

The introduction of polystyrene grafts into poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) film has been found to produce changes in the thermal properties of the grafted matrix because of the incompatibility of the two polymeric components.[13] The sulfonation of the grafted films further imparts considerable changes in the overall thermal stability of the membrane. The most important one is the desulfonation process occurring at elevated temperature that leads to loss in the ion-exchange capacity of membranes beyond $\sim$ 200°C, as reported in Part I.[14] The clear identification of the degradation products evolved at various temperatures offers the possibility to understand more precisely the mechanism of membrane degradation. For that purpose, the present investigation is aimed at evaluating the thermal behavior of graft copolymer membranes by thermogravimetry (TG) in combination with FTIR and mass spectroscopy. The evolution of various degradation products from a 40% grafted and subsequently sulfonated membrane during thermal treatment were monitored (He, 50–650°C), and a simple degradation model for this membrane is proposed.

EXPERIMENTAL

Materials

The two-step preparation of the cation-exchange membrane has been reported earlier.[6] In the first step, FEP film was grafted with styrene to produce FEP-g-polystyrene copolymer film. In the subse-

quent step, the grafted film was sulfonated to obtain FEP-g-polystyrene sulfonic acid (FEP-g-PSA) membrane. Prior to the TG analysis, the membrane was dried in a vacuum oven (1 Torr, 80°C) for 24 h and stored dust-free at ambient atmosphere for several days. The chemical composition of the membrane at room temperature was 55% FEP, 38% sulfonated polystyrene (93% of styrene units sulfonated), and 7% water.

Instrumentation

The TG–FTIR (TG/Plus, Bomem Inc.) is a programmable software-driven system that monitors sample temperature, sample weight, and up to 16 gases during a run, a wide range of which are precalibrated and selectable from the data base, e.g., in this investigation, H_2O, CO_2, CO, and SO_2. The schematic layout of the system is presented in Figure 1. A sample suspended in a flowing carrier gas (He) stream is subjected to a controlled heating ramp to induce thermal decomposition. The progress of the reaction is monitored continuously *in situ* by weight loss and its correlation with any evolved gases detected, identified, and estimated by FTIR. In the

ideal case, where all evolved gases are infrared-active, the system permits, in principle, a complete material balance for the decomposition process.[15,16]

In this study, a quadrupole mass spectrometer (Balzers QMA 125) was incorporated into the system to allow on-line detection of any infrared transparent gases, e.g., H_2, O_2, and N_2, with the secondary function to confirm product identity from FTIR. MS sampling was achieved by pumping a small fraction of the vent stream from the multiple-pass (8 m path length) IR gas cell (Fig. 1) through a heated capillary (2 m × 0.15 mm) with ultimate introduction to the MS analysis chamber via an intermediate pressure reduction valve (gas inlet system GES 010).

Methodology

A typical run in the TG–FTIR would be to load the membrane as cut pieces (~ 10–20 mg) and subject it to a linear heating ramp (10°C min^{-1}) in flowing He (150 mL min^{-1}) up to 650°C (typical run time 1 h). IR spectra (4 cm^{-1} resolution) were recorded every 30 s and automatically stored in the run file for later analysis. Evolution rates of up to 16 products (measured as % wt equivalent per minute based
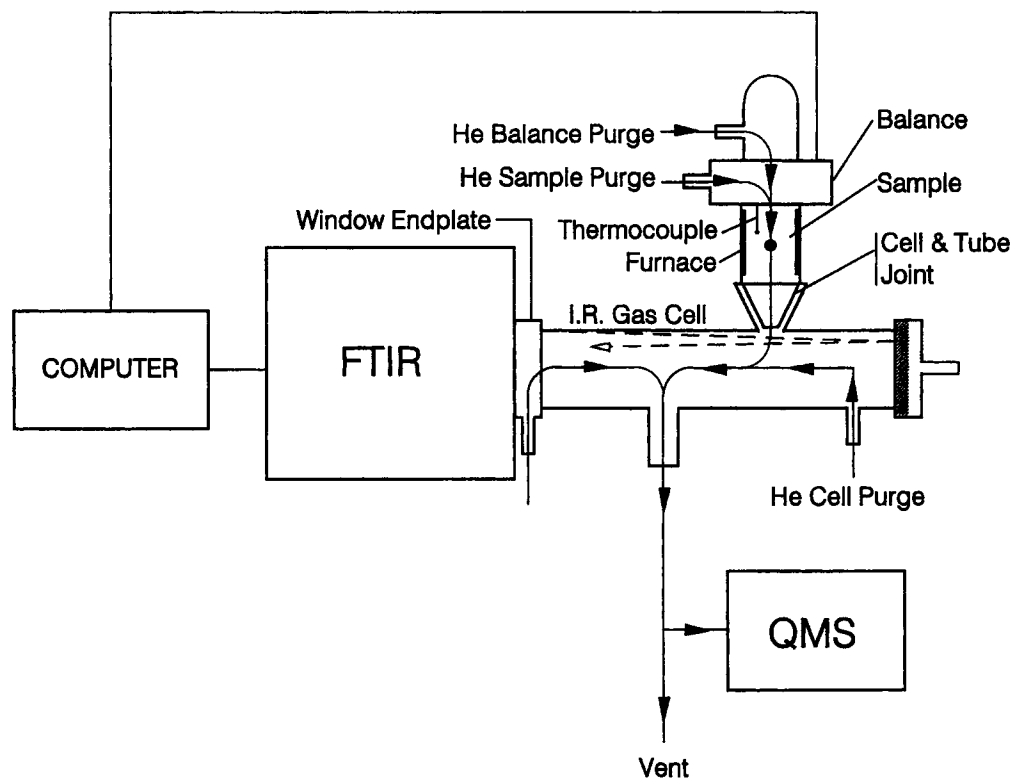
Figure 1   Schematic layout of the TG–FTIR/MS system.
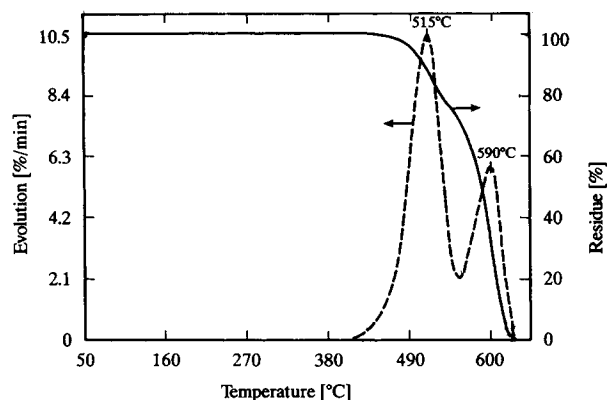
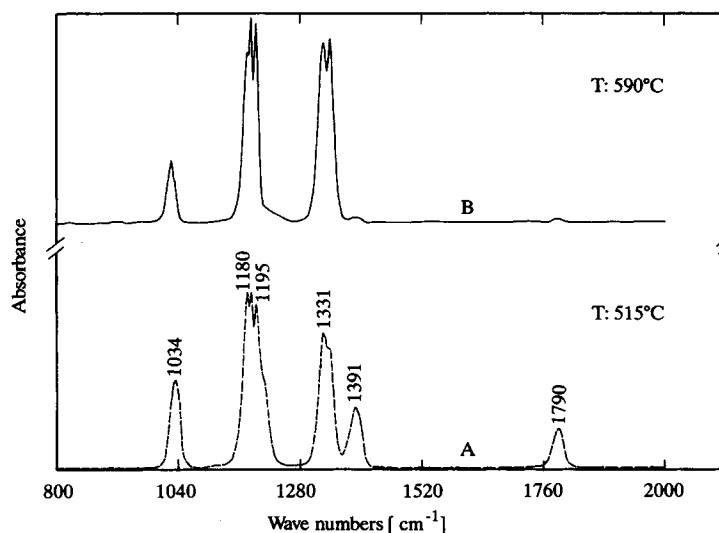**Figure 2** Gaseous evolution pattern in TG analysis of ungrafted FEP film.

on the starting weight) could be monitored with up to four being displayed in real time during the run, along with the balance reading and temperature.

RESULTS AND DISCUSSION

As already reported in Part I,[14] membranes obtained by the grafting of styrene onto FEP films, followed by sulfonation, have been found by TG analysis to show a multistep fragmentation pattern. Grafting of styrene introduces a two-step decomposition in the resulting FEP-g-polystyrene copolymer film, whereas subsequent sulfonation to produce membrane (FEP-g-PSA) results in a three-step degradation pattern tentatively attributed to dehydration, desulfonation, and degradation of the FEP back-

bone, respectively, with increasing temperature. Using here the coupled technique TG-FTIR/MS, the decomposition patterns obtained from TG analysis are reproduced and further correlated with the evolution of gaseous products.

The original FEP film shows decomposition starting around 450°C and can just be resolved (in the weight loss curve) into two contiguous steps (Fig. 2). The evolution pattern for generic organofluorine species (based on the IR band due to the C—F stretch in the range 1100–1000 cm^{-1})[17,18] shows this sequential process more clearly with evolution maxima at 515 and 590°C. It is of no great consequence that there is little quantitative relation between the evolution curve response and weight loss because of the nonspecificity of the reference and the known complexity in IR spectra of multiple F-substituted organics. However, inspection of the FTIR spectra in Figure 3 corresponding to the maxima shows that the evolving species are slightly different with extra bands (1391, 1790 cm^{-1}) appearing at 515°C, in addition to strong bands at 1034, 1180, and 1331 cm^{-1}, the latter two being attributable to the $=CF_2$ moiety.[17] The spectrum matches closely the reference library spectrum of hexafluoropropene C_3F_6,[19] and the bands at 1391 and 1790 cm^{-1} are attributed to the C—F stretch in —CF_3 and the C$=$C stretch, respectively, the latter being IR inactive in C_2F_4. MS was able to confirm the appearance of fragments of the general type C_xF_y ($x = 1$–3, $y = 1$–6) during the overall decomposition process above 500°C. The main peaks at 31 (CF$^+$), 50 (CF$_2^+$), 81 ($C_2F_3^+$), and 100 ($C_2F_4^+$) are characteristic of the major monomer component, C_2F_4,[20] whereas peak

**Figure 3** FTIR spectra of effluents of ungrafted FEP film at (A) 515°C and (B) 590°C.
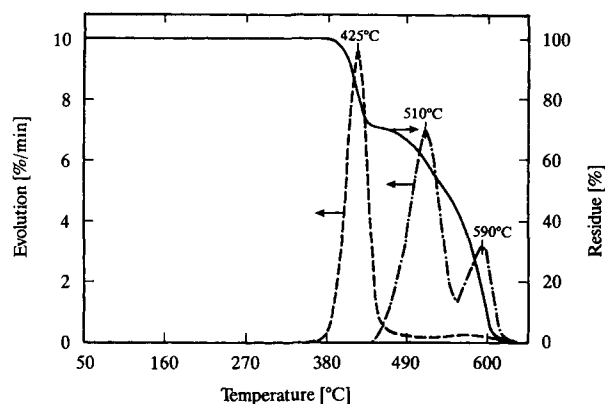
Figure 4 Gaseous evolution pattern in TG analysis of FEP-*g*-polystyrene copolymer film.

69 (CF_3^+) and a weak (parent) peak at 150 ($C_3F_6^+$) clearly originate from the minor level ($\sim$ 10 wt %) of C_3F_6 present in the FEP film.

The grafting of polystyrene into the FEP film simply introduces a new degradation step at a lower temperature. A typical pattern for an FEP-*g*-polystyrene graft copolymer film (40% grafted) is shown in Figure 4. The only new feature here compared to the ungrafted FEP is the weight loss above 400°C, which correlates with an evolution peak for generic "aromatics" [IR band envelope in the range 3100–3000 cm^{-1} (Ref. 17) based on a precalibrated toluene reference spectrum] at 425°C, but with a weak tail evolution extending up to $\sim$ 600°C. The best match

for the IR spectrum (Fig. 5) recorded at 425°C with the spectral database (Sadtler Libraries for Spectra Calc search module) was styrene, as expected, but with some weaker additional bands at 2941, 2866, and 1455 cm^{-1}, characteristic of a C — CH$_3$ grouping. MS confirmed the identity of evolved gas as a styrene monomer (parent peak at m/e = 104) but with no clear supporting evidence for any thermally induced derivatives, such as toluene and/or ethyl benzene. These observations, together with the consistency of the measured weight loss with the nominal polystyrene composition and the lack of any significant residue at the end of the run, suggest that the polystyrene component undergoes a relatively clean depolymerization process. This conclusion is supported by another study in the literature based on the pyrolytic chromatographic method.[21] Styrene was the predominant product (99.8%) of the thermal degradation of polystyrene at 430°C with only minor quantities of benzene, toluene, and ethyl benzene.

The thermal degradation behavior of an FEP-*g*-PSA membrane with a 40% degree of grafting is rather more complex than that of the foregoing precursor samples but can still be conveniently divided into four distinct stages (Fig. 6): In stage 1 (T = 50–200°C), there is only H$_2$O evolution in the form of an initial pulse but with the major fraction desorbing rather slowly above 100°C. The rapid loss is considered to represent preliminary removal of physisorbed H$_2$O, whereas the slow loss corresponds
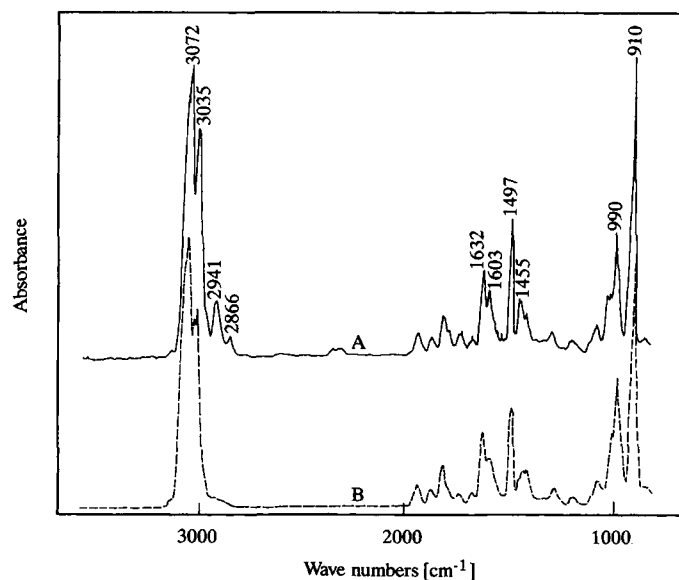
Figure 5 FTIR spectra of (A) effluents at 425°C of FEP-*g*-polystyrene copolymer film and (B) styrene monomer in Sadtler spectral database.
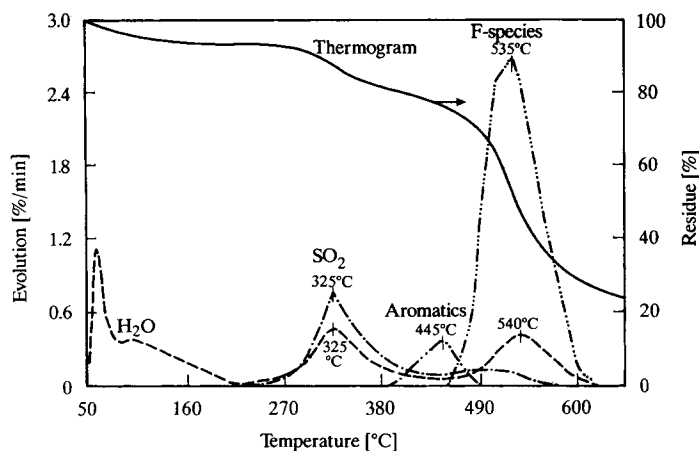
Figure 6   Gaseous evolution pattern in TG analysis of FEP-g-PSA membrane.

to desorption of H_2O, which is strongly bonded to the acidic sulfonate groups, as discussed in Part I.[14] In stage 2 (200–400°C), roughly half the total amount of SO_2 evolves [identified by the band envelope centered at 1360 cm^{-1} (Ref. 18)] together with H_2O in close correspondence, both showing peak maxima at 325°C. This suggests that both the fragments, SO_2 and H_2O, have a common origin in desulfonation.

Interestingly, the dearomatization process (stage 3, 400–500°C), i.e., loss of styrene, is markedly perturbed by the preceding desulfonation. Compared to the unsulfonated film (Fig. 4), styrene evolution (confirmed by inspection of the IR spectrum at 445°C) is markedly suppressed with a weight loss of only ~ 6–7% (inclusive of small levels of H_2O,

SO_2), i.e., at most only one-quarter of the expected value. It should be noted that SO_2 and H_2O continue to evolve, albeit at low levels, throughout this temperature range, as illustrated in Figure 6, which was simultaneously confirmed by MS. This implies that total desulfonation is a somewhat complex process, possibly involving corruption of (part of) the polystyrene component. Consistent with this view, there is a significant amount of residue (~ 25 wt % relative) after heating the membrane to 650°C, which approximately corresponds to the amount of styrene "missing" from the de-aromatization process (stage 3).

The FEP backbone degradation process is also to some extent affected insofar as the evolution of fluorocarbons now appears as almost a single feature
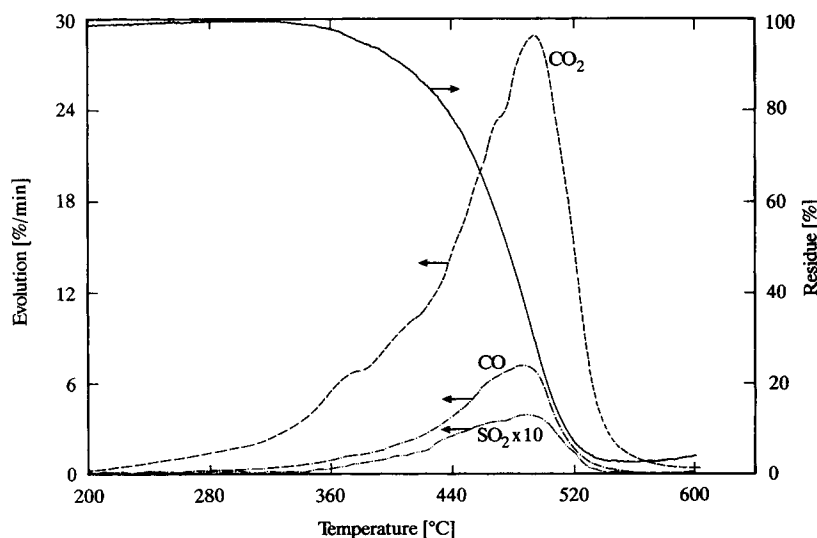
Figure 7   TG analysis of residual mass under oxygen (temperature-programmed oxidation, TPO).

at 535°C but with a weight loss ($\sim$ 50%) corresponding to the nominal composition. However, in this final stage of degradation (stage 4, $T = 500$–650°C), the information is unfortunately slightly obscured by the weak evolution of CO_2 (Fig. 6, not shown for clarity), which is suspected to originate from adventitious oxidation of a small part of the carbonaceous residue by traces of O_2 in the He car-
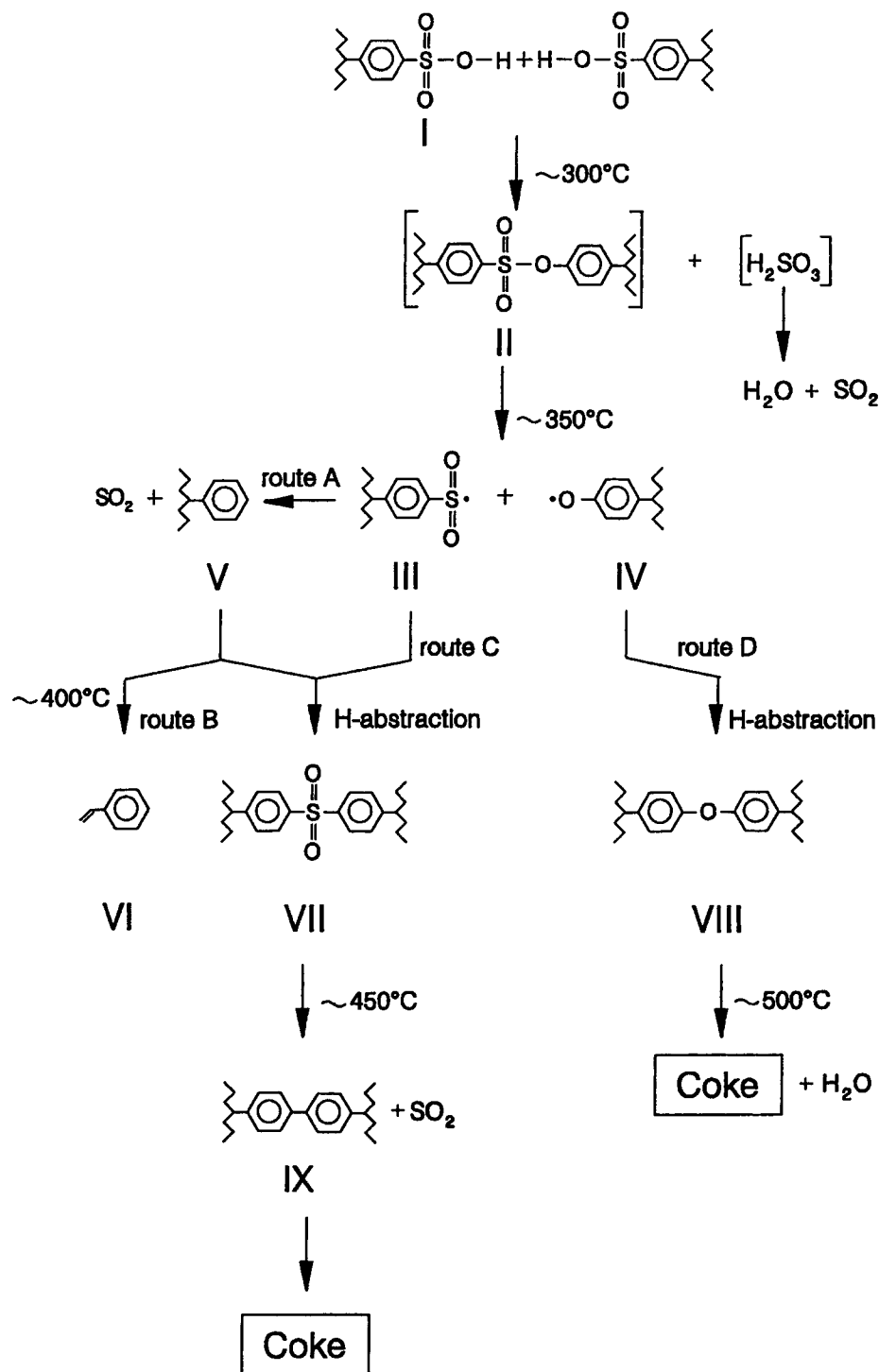
Figure 8 Schematic representation of the likely mechanism of FEP-g-PSA membrane degradation.

rier gas. Thus, the final evolution peak of H_2O (T_{max} ~ 540°C) cannot with complete confidence be attributed to bona fide pyrolysis although the integrated amount (~ 3.5 wt % as H_2O ≡ 0.4 wt % as H) far exceeds (~ ×8) that expected from oxidation of carbonaceous residue with a hypothetical stoichiometry C_1H_1, assuming that this is the origin of the measured CO_2 (~ 3 wt % ≡ 0.8 wt % C).

The residue was subjected to temperature-programmed oxidation (TPO, 20 vol % O_2) up to 650°C and showed evolution peaks of CO_2, CO, and SO_2 at ~ 500°C, with no discernible H_2O peak or fluorocarbons (Fig. 7). Integration of these peaks enabled an approximate compositional analysis, yielding 100 ± 10% C and 2 ± 0.2% S, i.e., the residue was essentially graphitic (no H content) with only a trace of S. This confirmed that desulfonation was virtually complete and suggests that substantial dehydrogenation of the styrene units occurs during pyrolysis.

Based on the foregoing results and correlation with data from the literature on similar polymer systems, a tentative model may be proposed for the thermal degradation of this sulfonated membrane in an inert atmosphere and is presented in Figure 8. The first stage (desulfonation) must involve H abstraction, presumably from a neighboring sulfonic acid group as depicted in **I**, resulting in a cross-linked sulfonate-bridged intermediate structure (**II**). The stoichiometry of the evolved products is formally equivalent to sulfurous acid, H_2SO_3, but this compound, if formed, would be expected to decompose rapidly at 350°C to yield simultaneously SO_2 and H_2O, as observed in Figure 6. Above 350°C, the polysulfonate structure **II** may undergo homolytic cleavage to give a radical sulfone (**III**) and a radical phenoxy group (**IV**). The former rapidly eliminates SO_2 to leave a polystyrene fragment (**V**) as per route A, which will subsequently depolymerize (route B). However, the major fraction of the polystyrene fragment (**V**) is likely to be rapidly scavenged by radical species **III** and **IV** to yield either a sulfone structure (**VII**, route C) and/or an ether (**VIII**, route D), both reactions implicitly requiring aromatic H atom abstraction. Good evidence exists in the literature that the proposed structures **VII** and **VIII** are thermally stable above 400°C.[22,23] The decomposition of polysulfone (**VII**) to a polybiphenyl (**IX**) is known to occur above 450°C (Ref. 24) and is probably responsible for the continuing evolution of SO_2 in this temperature range. The decomposition of the poly(phenyl ether) (**VIII**) with loss of H_2O (as observed) is reported to occur above ~ 500°C.[22] Both of these last-mentioned processes leave behind par-

tially dehydrogenated aromatic structures that are almost certainly precursors to coke,[25] i.e., the residue observed after depolymerization of the FEP backbone and volatilization of its monomer constituents, which is complete above ~ 600°C.

In conclusion, this study has advanced significantly our understanding of the thermal degradation characteristics of the radiation-grafted and sulfonated FEP-g-polystyrene membranes. The coupled analytical technique TG-FTIR/MS offers good prospects for increasing application in this research field. A likely future possibility is to investigate *ex situ* the effect on similar membranes of actual fuel cell operation and related problems of accelerated deterioration.[7]

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