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Attack of hydroxyl radicals to \(\alpha\)-methyl-styrene sulfonate polymers and cerium-mediated repair via radical cations†

Tom M. Nolte, †ab Thomas Nauser b and Lorenz Gubler a

Both synthetic polymers (membranes, coatings, packaging) and natural polymers (DNA, proteins) are subject to radical-initiated degradation. In order to mitigate the deterioration of the polymer properties, antioxidant strategies need to be devised. We studied the reactions of poly(\(\alpha\)-methylstyrene sulfonate), a model compound for fuel cell membrane materials, with different degrees of polymerization with OH radicals as well as subsequent reactions. We observed the resulting OH\(^{-}\)-adducts to react with oxygen and eliminate H\(_2\)O, the relative likelihood of which is determined by pH and molecular weight. The resulting radical cations can be reduced back to the parent molecule by cerium(III). This ‘repair’ reaction is also dependent on molecular weight likely because of intramolecular stabilization. The results from this study provide a starting point for the development of new hydrocarbon-based ionomer materials for fuel cells that are more resistant to radical induced degradation through the detoxification of intermediates via damage transfer and repair pathways. Furthermore, a more fundamental understanding of the mechanisms behind conventional antioxidants in medicine, such as ceria nanoparticles, is achieved.

Introduction

Oxidative stress is a critical lifetime-limiting factor for sulfonated polyaromatic proton exchange membranes (PEMs) in the polymer electrolyte fuel cell (PEFC). These ionomers are of interest to replace the widely used perfluorooalkylsulfonic acid (PFSA) membranes, owing to their much lower gas permeability, higher glass transition temperature, and potentially lower cost.\(^1\) Oxidative stress is created by the presence of radical species, such as HO\(^{\bullet}\), H\(^{\bullet}\) and HOO\(^{\bullet}\), which are formed during the operation of the fuel cell in the presence of H\(_2\)O, O\(_2\), and the noble metal catalyst.\(^2\)

The hydroxyl radical (HO\(^{\bullet}\)) can be particularly detrimental to the polymer as it initiates degradation. HO\(^{\bullet}\) reacts with aromatic compounds with typical rate constants in the range of the diffusion limit of \(10^9-10^{10} \text{ M}^{-1} \text{ s}^{-1}\).\(^3,4\) However, the nature of follow-up reactions, intermediates and the associated kinetics are rarely considered. The final result of HO\(^{\bullet}\) attack may be chain oxidation (e.g., hydroxylation), crosslinking, or chain fragmentation.\(^5\) These different mechanisms of polymer aging depend on the chemistry of the polymer. Thus, strategies to prevent aging ought to take these pathways into account (Fig. 1). For example, ‘repairing’ intermediates formed upon radical attack may be accomplished with suitable additives, i.e., antioxidants (e.g. in Fig. 1, reaction 11).\(^6\)

There is an analogy to oxidative stress in living cells: here, it is the characteristic of imbalance between reactive oxygen species (ROS) generation and an organism’s endogenous defenses. OH\(^{\bullet}\) is generated from ‘leakage’ of electrons along the cellular electron transport chain, and can react with cell constituents (DNA, proteins). As a consequence, oxidative stress is the basis of many serious diseases such as cancer. Nature has its way of detoxifying radicals, i.e., using vitamins and enzymes. When these endogenous mechanisms to combat oxidative stress fall short, we can consider treatment via synthetic alternatives. Ceria nanoparticles (CNPs) are promising inorganic antioxidants for many biomedical applications. CNPs have demonstrated antioxidant enzyme-mimetic activity, as well as the capacity to scavenge a variety of ROS in both cell and animal models. Concomitantly, a reduction in DNA damage (e.g. in lung cells) has been observed.\(^7\)

Cerium ions or ceria particles are also used to mitigate degradation in PFSA-type fuel cell membranes\(^8\) via direct scavenging of OH\(^{\bullet}\), and potentially H\(^{\bullet}\).\(^9,10\)

\[
\text{Ce}^{3+} + \text{HO}^{\bullet} + \text{H}^+ \rightarrow \text{Ce}^{4+} + \text{H}_2\text{O} \quad (k_1 = 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1})
\]  

(1)
The antioxidant properties of CNPs are dependent, also, on the ability to undergo redox cycling between the valences Ce³⁺ and Ce⁴⁺ ions (as CeO₂₋₋₂) on the surface of CeO₂ or Ce₂O₃ CNPs in aqueous solution.¹¹ Radical scavenging by Ce³⁺ is very effective in PFSA membranes, because the lifetime of HO⁻ is on the order of microseconds, thus with a relatively small concentration of Ce³⁺ of ~0.1 M over 90% of HO⁻ are quenched.³ The ratio of Ce⁴⁺ to Ce³⁺ is influenced by the chemistry of the medium. For example, H₂O₂ and HOO⁻, which are also present in a fuel cell membrane,¹² can reduce Ce⁴⁺ to Ce³⁺:¹³

\[ \text{Ce}^{4+} + \text{H}_2\text{O}_2 \rightarrow \text{Ce}^{3+} + \text{HO}_2^- + \text{H}^+ \quad (k_2 = 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}) \tag{1} \]

\[ \text{Ce}^{4+} + \text{HO}_2^- \rightarrow \text{Ce}^{3+} + \text{O}_2 + \text{H}^+ \quad (k_3 = 2.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}) \tag{2} \]

Because the Ce⁴⁺ that is formed reacts with H₂O₂ and HOO⁻, the scavenger Ce³⁺ can effectively be restored. Thus, these regenerative reactions enable a more effective catalytic HO⁻ scavenging mechanism by Ce³⁺. In polyaromatic fuel cell membranes, however, owing to the very fast reaction with the aromatic units, the lifetime of HO⁻ is in the nanosecond range, thus around 3 orders of magnitude shorter than in PFSA membranes. Therefore, protecting polyaromatic polymers by scavenging of HO⁻ alone is not sufficient.⁶ Nevertheless, we might exploit the redox cycling mechanism of Ce that forms the basis of its medicinal properties: we propose to use the Ce⁴⁺/Ce³⁺ redox couple to ‘repair’ the damage to polyarylene type ionomers caused by attack of the OH⁻ radical. The question in this context is, given the chemistry of the polymer: does an intermediate exist that is sufficiently long-lived to be amenable to repair?

An intermediate formed as a result of OH⁻ attack on arylene is the aromatic radical cation (Ar⁺⁺) (compound E, Fig. 1), produced by acid-catalyzed elimination of H₂O (reaction 9, Fig. 1) from the OH-adduct (compound B, Fig. 1).¹⁵,¹⁶ Since proton exchange membrane fuel cells operate under acidic

![Reaction pathways considered in this study. Reaction between the PAMSS polymer/oligomer (compound A) with OH⁻ (reaction 5), produces a hydroxycyclohexadienyl adduct (compound B). This adduct can undergo (acid-catalyzed) elimination of H₂O (reaction 4) to produce a radical cation (compound E). Short-lived intermediates of PAMSS (≤1 ms) are indicated in color. The aim of this study is to determine whether Ce³⁺ is a competitive repair agent for the radical cation (reaction 11), in terms of side reactions (reaction 7, 8 and 12–14).]
conditions, elimination of H2O is usually fast.15-17 The redox potential E° of Ce4+/Ce3+ of 1.44 V18 is favorable as compared to E°(Ar3+/Ar) = 2.0-2.4 V.19 In previous work using poly-
(π-methylstyrene sulfonate) (PAMSS) oligomers as model aromatic compound, we found that the lifetime of the radical cation increases with the degree of polymerization, potentially due to π–π interactions, and does not produce benzyl radicals due to the presence of the π-methyl group.20 PAMSS is well soluble in water making it a viable candidate to study the kinetics of its reaction with Ce3+ in aquo. PAMSS represents a constituent of a fuel cell membrane. Though other models compounds representing polyarylene type polymers (e.g. polysulfones) are conceivable, they are beyond the current scope.

In the work reported here, we studied the interaction (reaction 11, Fig. 1) between Ce3+ and the aromatic radical cation of PAMSS (compound E) to investigate whether cerium could function as a regenerative antioxidant for repairing aryl-type polymers. To determine whether the repair pathway is viable we compared the regeneration kinetics with a potential side reaction, prominently, the reaction of the HO-adduct (compound B) with O2 (reactions 7–7 and 8, Fig. 1). The degree of polymerization of PAMSS was varied from 1 to 1700 in order to study the effect of Ar° lifetime and redox properties. The results of this study are of high relevance to material scientists and engineers looking to improve the durability of hydrocarbon based fuel cell membranes, as well as for medicinists aiming to elucidate and optimize antioxidant mechanisms.

Materials and methods

PAMSS oligomers/polymers (> 95% sulfonation degrees) with molecular weights M0 of 2660, 14 600, 73 800 and 354 000 Da, and polydispersity indices of <1.5, <1.2, <1.2 and <1.2, respectively, were supplied by PSS (Polymer Standards Service, Mainz, Germany). A ‘monomeric unit’ of PAMSS, 4-tert-butylbenzenesulfonyl, was used to represent a ‘degree of polymerization’ of 1. Ce3+ was added as a salt, Ce2(SO4)3, obtained from Sigma-Aldrich (≥99.99% purity). Water from a Millipore-Q system was used to prepare solutions that were saturated with O2, N2, O2, or Ar depending on the reaction studied. Samples were gas saturated in Schlenk-tubes which were repeatedly evacuated to 10 mbar and refilled (a minimum of 3 repeats) with the desired gas. The solutions were transferred from a gas-tight syringe (10 ml, Hamilton, SampleLock, Bonaduz, Switzerland) to the measurement cell via a syringe pump. Acidic pH was adjusted with H2SO4 (95-97% purity), while solutions at pH 7 were buffered with 0.1 mM phosphate buffer (NaH2PO4·H2O, >99% purity), unless stated otherwise. Experiments were carried out at room temperature (25 °C). tert-Butanol was obtained from Merck (Darmstadt, Germany) and was used to scavenge OH* when needed.

Pulse radiolysis

Pulse radiolysis experiments were carried out using a Febetron 705 (Titan Systems Corp., presently L-3 Communications, San Leandro, CA, USA), equipped with an optical detection system. For details see Nauser et al. (2008).21 Irradiations were performed in a 6 cm quartz cell (Hellma, Müllheim, Germany) with <50 ns pulses of 2 MeV electrons. The dose was measured using a thiocyanate dosimeter.

Production of OH* radicals

Pulse irradiation of water results in the formation of primary species with yields G(OH*) [primary yield (molecules per 100 eV), pH 7], G(¢eaq) and G(H+) of 2.7, 2.65 and 0.6,22-24 respectively, whereby G = 1 equals to 0.1036 μmol of a species generated per 1 J kg⁻¹ absorbed energy. The solutions were saturated with N2O (22 mM) to increase the OH* yield and reduce side reactions. The solvated electron, eaq, reacts with N2O to yield additional OH*:

\[ \text{N}_2\text{O} + e_{\text{aq}}^- + \text{H}_2\text{O} \rightarrow \text{N}_2 + \text{OH}^+ + \text{OH}^- \]

\[ (k_4 = 9.1 \times 10^7 \text{ M}^{-1} \text{s}^{-1}) \] (4)

Reaction of OH* with PAMSS

Reaction of OH* with an aromatic unit (Fig. 1, reaction 5) produces a hydroxycyclohexadienyl adduct (Fig. 1, compound B).20,25 Here, we quantified the rate constants for the reaction between the polymers and OH*:

\[ \text{OH}^* + \text{PAMSS} \rightarrow \text{PAMSS}(-\text{OH})^* \] (5)

PAMSS radicals have relatively low extinction coefficients and side-reactions might be involved at high concentrations of radicals. To bypass and minimize this, we studied the reaction with OH* via competition with Fe(CN)6^4-:

\[ \text{OH}^* + \text{Fe(CN)}_6^{4-} \rightarrow \text{OH}^- + \text{Fe(CN)}_6^{3-} \]

\[ (k_b = 1.05 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}) \] (6)

At relatively low dose (~10 Gy), the concentration of Fe(CN)6^4- was ~50 μM and the concentration of PAMSS was varied. Under N2O saturated conditions the radiation chemical yield (G) of OH* is ~5.6 × 10⁻⁷ mol J⁻¹ and is unaffected by the PAMSS concentration (dilute solutions, ≤100 μM). Thereby, the absorbance at 420 nm (Fe(CN)6^3-, ε420 = 1040 M⁻¹ cm⁻¹) is solely affected by the PAMSS concentration via competition for OH*. The absorption at 420 nm, virtually constant after ~5 μs, was measured.

Control experiments were performed using different dose/Fe(CN)6^4- ratios, as well as direct observation (details in the ESI†).

Reaction of hydroxycyclohexadienyl radicals with oxygen

Reaction of O2 with hydroxycyclohexadienyl radicals (Fig. 1, reaction 7) produces an Ar–OH(O2) radical adduct (Fig. 1, compound C):

\[ \text{PAMSS}(-\text{OH})^* + \text{O}_2 \rightarrow \text{PAMSS}(-\text{OH})(-\text{O}_2)^* \] (7)
effect on the kinetic trace of hydrocyclohexadienyl radicals. Mixtures of N₂O/O₂ were used and the concentration of O₂ in the samples was determined via the partial pressure of O₂ and its solubility in water (1.25 mM at 1.0 atm). O₂ concentrations ranged from 0 to 1.25 mM. Doses applied were ~40 Gy. All experiments reported were reproduced at least five times.

The characteristic λmax for hydrocyclohexadienyl-type radicals is ~325 nm, Fig. 2. However, other species, among which the Ar–OH(–O₂) radical adduct, absorbs also in this spectral range (Fig. 2B). Moreover, the addition of oxygen is reversible25,26 with an equilibrium constant K on the order of ≥10³ M⁻¹, because the reverse reaction is relatively slow (reaction −7, Fig. 1, with k₋₇ = 4.5±0.9 × 10⁻³ s⁻¹ as an upper limit for poly(styrene sulfonate) (PSS)²⁵). The addition reaction was monitored at λ = 360 nm, chosen empirically such that both the relative absorption of the OH•-adduct (relative to the Ar–OH(–O₂) adduct) and absolute absorption are maximized (Fig. S4B, ESI†). Based on earlier results²⁵,²⁶ we identified the decay within ~10–20 μs of the absorption maximum. The kinetic traces were fitted with pseudo-first order functions. This analytical setup minimized the need to fitting to equilibria or taking into account side reactions, such as *OOH elimination (reaction 8, Fig. 1, with k₈ = 2.7(±0.3) × 10³ s⁻¹ for PSS²⁵) to form a stable hydroxylated product (compound D). Thus, we can fit kinetic traces for the OH•-adduct with minimal interference.²⁵

Control experiments were performed using gas mixtures of Argon/O₂ and N₂/O₂ under low doses (~10 Gy) to characterize the relevance of the yield of OH•-adducts (details in Fig. S8, ESI†) on the apparent rate constants.

**Production of radical cations and reaction with Ce³⁺**

Under N₂/O₂ conditions and pH ~7 the yield of radical cations from OH•-adducts (e.g. via reaction 9, Fig. 1) is low: 0.1–1 μM for Mₚ = 354 000 Da (Fig. 2A, λmax ≥ 560 nm), and below our detection limit for smaller polymer weights. When the radical cation was produced at pH ~7 via elimination from the PAMSS-OH• adduct (Mₚ = 354 000 Da), no reaction between the radical cation and Ce³⁺ was observed.

Rate constants for the elimination of OH•/H₂O have previously been identified as ~10⁴ s⁻¹ for a range of aryl-type OH•-adducts,¹⁶ whereas for the reaction between radical cation and H₂O (reaction −9, Fig. 1) values differ 10¹⁻¹⁰⁷¹⁶ (k₋₉ = 1–2 × 10⁴ s⁻¹, Fig. 5 and Fig. S10–S12, ESI†). Thus, simultaneous production of radical cations via elimination (reaction 9, Fig. 1) from the PAMSS-OH• adduct (Fig. 2A) might obscure the depletion via reaction with Ce³⁺ (reaction 11, Fig. 1).

Bypassing the H₂O/OH⁻ elimination from PAMSS-OH• route, radical cations were produced by electron transfer to sulfate radicals (reaction 10, Fig. 1):

\[
PAMSS + SO₄²⁻ \rightarrow PAMSS⁺ + SO₄²⁻ \quad (k₁₀ = 0.6–1.0 × 10⁹ M⁻¹ s⁻¹) \quad (8)
\]

Potassium peroxodisulfatesulfate (50 mM) was added to argon-saturated solutions at pH ~2 (adjusted with H₂SO₄). Dose was ~100 Gy, and tBuOH (100 mM) was added to scavenge the primary OH• radicals. Concentrations of PAMSS were used according to the degree of polymerization (e.g. 4.5 mM for PAMSS-354 000). We varied the Ce³⁺ concentration to obtain pseudo first-order rate constants for the reaction:

\[
Ce³⁺ + PAMSS⁺ \rightarrow Ce⁴⁺ + PAMSS \quad (k₁₁) \quad (9)
\]

**Results and discussion**

**Reaction of OH• with PAMSS**

The introduction of PAMSS to a solution containing Fe(CN)₆³⁻ led to a decrease in the absorption recorded at 420 nm (i.e. reaction between Fe(CN)₆³⁻ and OH•). This is indicative of a reaction between OH• and PAMSS (i.e. a competition for OH•). Taking into account reaction 6 (Fig. 1, Fe(CN)₆³⁻+ OH•) we fitted the data (blue lines and triangles in Fig. 3) to obtain k₅ = 5.7(±0.2) × 10¹¹ M⁻¹ s⁻¹ for the bimolecular reaction rate constant between PAMSS-354 000 (the polymer with the highest Mₚ) and OH• (Fig. 1, reaction 5). By extension, we obtained the following data for the series of oligomers/polymers with different molecular weight, given in Table 1.
The apparent yield of adducts (absorption at 360 nm) under N₂O atmosphere is less than twice that obtained under O₂ (3.2 and 5.9 absorbance Gy⁻¹, resp.), i.e. G(N₂O)/G(O₂) = 1.86 ± 0.04 (Fig. 4A). The ratio in yields of the primary radicals, G(ØH), G(N₂O) + G(H, N₂O) = 0.622 and G(ØH*, O₂) + G(H, O₂) = 0.342, i.e. G(N₂O)/G(O₂) = 1.82, is similar. We infer that the absorption corresponds to 5–10% PAMSS-ØH adducts. Nevertheless, measurement of k₅ via direct observation produced the same value as obtained via competition kinetics (Table 1), Fig. S1 (ESI†). The suite of control studies indicated the stability of the method (Table 1).

We obtained larger values for k₅ for larger molecular weights. However, when we express k₅ per monomer unit, there is a notable decrease. The data match earlier observations by, e.g., Dockheer et al.²⁰ for a more limited range of Mₘ (Table 1); we find our values either slightly lower or equal to what has been reported.

The influence of size could be expressed as k₅ ~ [n]²⁰±₀·⁰₈ (k₅ ~ [n]²⁰⁻³⁷ including Dockheer et al. data²⁰ Fig. 6), wherein [n] is the degree of polymerization. Variation in the polydispersity index (PDI) between the polymers is not expected to influence the relationships obtained in this study (since PDI < 1.2). The “reaction exponent”, here 0.60 ± 0.08, is sometimes defined as ₀²⁷⁻²⁸

\[
\theta = \frac{(3 + g)}{2}
\]  

In case the polymer dynamics are ‘Rouse-like’ (single un-entangled chain; no significant interactions between chain segments) z = 4. In turn, g = 0 represents a non-interacting electron–electron system (the correlation hole ²⁹ is screened out). Then, the reaction exponent is (3 + 0)/4 = 0.75. Indeed, k₅ values are near the “diffusion control” k₅ ~ [n]²⁰⁻⁰, i.e. 0.60 ± 0.08 ≤ 0.75. Thus, k₅ is largely independent of the reactivity of the reaction site.

**Decay of hydroxycyclohexadienyl radicals**

The first order decay of PAMSS-ØH⁺ seems to be a function of the yield of OH⁺-adducts (Fig. 3S and 8S, ESI†). If we assume the yield of OH⁺-adducts is 8 times larger under 40 Gy and N₂O, as compared to under 10 Gy and argon, we derive based on Fig. 3S and 8S (ESI†) a slope (rate constant) on the order of 5 × 10⁻¹⁰ M⁻¹ s⁻¹ (Fig. 3S, ESI†). The intercept is 2.2(±0.3) × 10⁹ s⁻¹ (Fig. 3S, ESI†). The half-life of the PAMSS-ØH⁺ adduct (as observable at 325 nm) generally increased with Mₘ (e.g. kₙₘₐₓ = 1.4(±0.3) × 10⁹ s⁻¹ and 6.1(±0.3) × 10⁸ s⁻¹ for Mₘ = 2660 and 14600, resp.), though quantification requires the relative (effective) concentration of OH-adducts for different Mₘ. PAMSS-ØH⁺ adducts seem to be more stable as the Mₘ increases.

A neighboring monomer might interact with the radical site in such a way that its intrinsic reactivity is lowered, or the
Upon exposure of the hydroxycyclohexadienyl radicals to O$_2$ we observed a shift to shorter wavelengths over time (Fig. 2B). The shift to shorter wavelength for reaction products under O$_2$ atmosphere (Fig. 2B and Fig. S4–S6, ESI†) has been observed in related studies and is attributed to O$_2$-radical adducts.

The yield of OH*-adducts varied for different ratios of N$_2$O/O$_2$ and between pulses (Fig. 4A); the concentration of OH*-adducts under N$_2$O/O$_2$ mixtures was directly proportional to the yield of OH*, see Fig. 4A and Fig. S7 (ESI†). This was taken into account when evaluating the pseudo-first order reaction with O$_2$ (reaction 7, Fig. 1). We consider the relative concentrations of OH*-adducts. Thus, Fig. 4A was corrected for the adduct yields (maximum absorbance, at ~2 μs), to give Fig. 4B.

Control studies indicated the stability of the method (Fig. S8, ESI†): H* is quenched by PAMSS, rather than O$_2$. There is no difference between the $k_t$ values obtained from series under argon or N$_2$O. Therefore, PAMSS-14 600(-H*) adducts react slower with O$_2$ than do PAMSS-14 600(-OH*) adducts and do not contribute significantly to the result. Different initial yields of PAMSS-14 600(-OH*) adducts (at $t = 2$ μs), do not appear to affect the results (Fig. 4C and Fig. S8, ESI†). Thus, in the range of 2 μs to 10–20 μs, there is no measurable equilibration or elimination of OOH* yet. Compared to 1.25 × 10$^{-3}$ M for O$_2$ (in O$_2$ saturated solutions), the experimental series may also yield superoxide, O$_2^*$ (Fig. S8-1A, ESI†), in 10 μM (higher-end estimation). In O$_2$ saturated solutions (~1.25 mM) G(OH*) ~ 2.8 × 10$^{-7}$ mol J$^{-1}$ and G(O$_2^*$) ~ 3.4 × 10$^{-7}$ mol J$^{-1}$. The reaction between PAMSS-OH and O$_2$ is thermodynamically favored (compared to that with O$_2$*) based on the energies of their frontier orbitals: $\Delta E \sim 0.4$ eV < $\Delta E$ < 0.9 eV (in-house calculation). The influence of O$_2^*$ has not been reported in related studies (under high O$_2$ concentrations). Thus, the reaction between O$_2^*$ and PAMSS-OH is of minor importance, and the rate constants for addition of O$_2$ obtained in this study can be considered accurate.

From fitting we obtained a rate constant $k_t$ = 4.8(±0.4) × 10$^6$ M$^{-1}$ s$^{-1}$ for the reaction between PAMSS-14 600(-OH*) and O$_2$ (see ESI† for other $M_n$) in Fig. 4C. The reaction of a carbon-centered radical with O$_2$ to form the corresponding peroxyl radical generally proceeds with a rate constant on the order of 10$^9$ M$^{-1}$ s$^{-1}$. However, because of electron delocalization in allylic and dienyl C-centered radicals, oxygen binds relatively weakly, which results in slower and reversible O$_2$ addition. These notions are in agreement with the data obtained. Other factors explaining the relatively low rate constants include steric hindrance ( tert-butyl) and polarity (sulfate) but need to be studied in more detail.

There appeared to be an influence of molecular weight, as $k_t$ of 2.2(±0.3) × 10$^7$ M$^{-1}$ s$^{-1}$ was found for the 4-tert-butylenznesulphonate (-OH*) adduct. The data are in the same order as was found for PSS-1100(-OH*): $k_t$ = 3.0(±0.5) × 10$^7$ M$^{-1}$ s$^{-1}$. For the reaction between the OH*-adducts and O$_2$, $k_t$ scales with $n$: $k_t$ ~ [n]^{-0.26±0.07}. PSS data might be included in the analysis if no significant influence by the extra methyl group is expected on the reaction thermochemistry, relative to the effect of $M_n$ (Fig. 6). The influence of polymer size on the reaction between PAMSS(-OH*) and O$_2$ (~0.26 ± 0.07) is different (2σ) from for the reaction between PAMSS and OH* (0.60 ± 0.08).
Since there is only 1 reactive site on the polymer, no relationship with \( n (k \sim [n]^p) \) should be expected if diffusive or quantum-chemical effects are absent. Instead, the polymer dynamics i.e. diffusive pathway (z) and/or quantum-chemical properties (g) (eqn (10)) are affected (<0) by the breaking of aromaticity by OH* to produce the hydroxycyclohexadienyl radical. It is worth noting that hydroxycyclohexadienyl radicals are relatively electron-rich and non-planar (Fig. 1, compound B), which would disfavor \( \pi-\pi \) interaction.

**Decay of radical cations**

In argon-saturated conditions and \( \text{pH} \sim 2 \), \( \text{SO}_4^{2-} \) radicals were produced from the reaction between peroxodisulfate and the solvated electron. \( \text{SO}_4^{2-} \) radicals oxidize PAMSS to produce a radical cation observable at 560 nm. We detected radical cations for \( 2600 \geq M_w \geq 354000 \), whereas for the 4-tert-butylenesulfonate (i.e. the monomer unit) no radical cations could be observed. The half-life of the radical cation was found to be \( \sim 40 \) to \( \sim 100 \mu s \) depending on the chain length (Fig. 5). The influence of size was reported earlier by Dockheer et al. for a more limited range of \( M_w \).

The radical cations showed longer lifetimes upon increasing the molecular weight of the polymer (Fig. 6 and Fig. S10 and S11, ESI†), with reaction exponents (\( k \sim [n]^{0.89 \pm 0.03} \)) similar to those for the reaction between the radical cation and \( \text{Ce}^{3+} \) (\( 0.12 \pm 0.01 \)). Extrapolation of the data recorded in absence of \( \text{O}_2 \) (under Ar), using a power function in Fig. 6 results in \( k = 1.6 \times 10^4 \text{ s}^{-1} \) for the first-order decay of the 4-tert-butylenesulfonate radical cation (\( \sim 40 \mu \text{s half-life} \)). This is relatively low compared to simple arenes, or even tert-butylenesulfonate (\( 10^5-10^6 \text{ s}^{-1} \)). The mode of decay by the radical cations is uncertain. The \( \alpha \)-methyl group prevents formation of a benzyl radical via a proton elimination (splitting) reaction and, instead, elimination of the sulfate was suggested or dealkylation (scission), Fig. 1. The cation might react intramolecularly with a nearby monomer, requiring a \( k \) of \( 10^6-10^7 \text{ s}^{-1} \). This is unlikely based on thermodynamic grounds, and it would likely result in a shift in \( \lambda_{\text{max}} \) (for a similar radical cation), which was not observed. A radical–radical reaction would involve rate constants in the range of \( 10^8-10^9 \text{ M}^{-1} \text{ s}^{-1} \) (diffusion-limited, no thermodynamic arguments). This mechanism does not explain the size dependence observed and the decay that is still observed at very low concentrations, \( \sim 10^4 \text{ s}^{-1} \). Rate constants for addition of \( \text{H}_2\text{O} \) to the radical cation (i.e. the backward reaction \( \sim 9 \), Fig. 1) to form the water adduct are on the order of \( 10^9 \text{ M}^{-1} \text{ s}^{-1} \). The decay observed in acidic aqueous solution is given by \( k = 6 \times 10^3-6 \times 10^4 \text{ s}^{-1} \). Addition of \( \text{H}_2\text{O} \) to the radical cation would occur via direction of the lone pair into the SOMO of the radical cation. The cation, and by extension the energy of this SOMO, could be subject to
The influence of Ce$^{3+}$ was attributed to the reduction of the pseudo-first order reaction rates and H$_2$O (previous section), similar to that observed for the reaction between the radical cation/C$_0$ as compared to pH

ESI Fig. 1). Minor bleaching was observed in some cases (Fig. S11A, radical cation back to the starting compound (reaction 11, rate constants were obtained, excluding the 4-tert-butylbenzenesulfonate (n = 1), the radical cations produced from the oligomers/polymer were exposed to Ce$^{3+}$. For all molecular weights, a decrease in the lifetime of the radical cation was observed with increasing Ce$^{3+}$ concentration. The influence of Ce$^{3+}$ was attributed to the reduction of the radical cation back to the starting compound (reaction 11, Fig. 1). Minor bleaching was observed in some cases (Fig. S11A, ESIF), potentially due to reaction –1 (cf. Fig. 1). From the plot of pseudo-first order reaction rates versus concentration, reaction rate constants were obtained, e.g. for the PAMSS-14600 radical cation in Fig. 5 we obtained $k_{11} = 3.9(±0.2) \times 10^6$ M$^{-1}$ s$^{-1}$ (see ESIF for other $M_\text{w}$).

As a validation exercise, experiments were conducted for a lower PAMSS (73 800) and higher persulfate concentrations, as well as under higher pH (Fig. S12, ESIF). The same value for $k_{11}$ was obtained for the series when fitting the kinetic traces over a short time regime, indicating the stability of the method. Nevertheless, the observed rate constants are higher at pH $\sim$ 3, as compared to pH $\sim$ 2. An offset of 2.9(±0.2) $\times 10^6$ s$^{-1}$ between regressions for pH $\sim$ 3 and pH $\sim$ 2 was obtained. The offset is partially attributed to the acid–base equilibrium (reaction, 9/–9, Fig. 1) (see previous section).

The influence of molecular weight on the reaction between the PAMSS radical cation and Ce$^{3+}$ was considered. The ‘reaction exponent’ is $-0.12 \pm 0.01$, i.e. $k_{11} \sim [n]^{-0.12\pm0.01}$. The value is similar to that observed for the reaction between the radical cation and H$_2$O (previous section), $-0.09$ (Fig. 6). The negative values support the interpretation that the thermochemistry of the radical cation is affected intramolecularly. Intramolecular charge–radical stabilization has already been confirmed on a fundamental level: chemical reactivity is controlled by radicals flanking the charged groups or by charged groups flanking the radicals. For the radical cations, too, a significant stabilization is implied, which may be expressed as $\theta < 0$, eqn (10). The radical cation is initially produced on the outer ‘surface’ of the polymer coil with a high degree of polymerization (diffusion limited). Quantum-chemical stabilization (g, eqn (10)) can be a $\pi$-donation into the outer-surface cation hole (i.e. the electron deficiency), effectively delocalizing (transferring) the cation hole to center of the polymer. It is conceivable that the polymer dynamics (z, eqn (10)) are also affected, for example, through bridging between polymer segments to facilitate radical stabilization.

Extrapolation of the data resulted in $k_{11} = 6.4(±0.7) \times 10^8$ M$^{-1}$ s$^{-1}$ for the reaction between 4-tert-butyl-benzenesulfonate radical cation and Ce$^{3+}$ (Fig. 6). No literature data could be found for reactions of Ce$^{3+}$ with aromatic radical cations. However, the ferrous ion (Fe$^{2+}$) reacts with (reduces) the radical cation of anisole with a rate constant of $k = 6 \times 10^8$ M$^{-1}$ s$^{-1}$ (pH 1.0) and with pseudocumene and isodurene radical cations with $k = 6(±1) \times 10^7$ M$^{-1}$ s$^{-1}$ (pH 2.5–3.5). These reactions are dependent on the ionic strength of the solution and, potentially, the polarity of the cation (Nolte et al., in prep.).

**Conclusion**

The reaction between PAMSS and OH$^*$ borders the diffusion-limit, resulting in the formation of hydroxycyclohexadienyl, i.e. OH radical adducts, Ar(–OH$^*$). These adducts can react with O$_2$, $k_r = 3 \times 10^8$ M$^{-1}$ s$^{-1}$, depending on the molecular weight, to produce O$_2$ adducts. Even though Ar(–OH$^*$) reacts with O$_2$, the effectiveness of this reaction depends on the thermodynamic equilibrium of H$_2$O elimination/addition, which is a function of pH. Under acidic conditions, the OH-adduct eliminates H$_2$O to form a radical cation. The polymeric radical cation was shown to react with Ce$^{3+}$ with rate constants of $3.5 \times 10^8$ M$^{-1}$ s$^{-1}$ influenced by intramolecular stabilization, likely including radical–charge (π–π) interaction. Radical cations could not be observed for the monomeric compound (4-tert-butyl-benzenesulfonate), for which no intramolecular stabilization is possible, potentially also due to the fast backward reaction (H$_2$O addition). The competition between the reaction pathways involving Ce$^{3+}$ (the repair reaction) or O$_2$ (as an indicator for irreversible damage) can be fine-tuned by modifying the size and structure of PAMSS with its effect on both steric/clustering and redox properties, with the ‘repair’ reaction with Ce$^{3+}$ generally being more efficient (compared to O$_2$) for shorter polymer chains.

The results of this study show that repair and stabilization of polymeric radicals can be achieved using cerium ions and neighboring groups via suitable thermochemical and kinetic interactions. This has ramifications for the design of durable areylene type fuel cell membranes and polymeric materials in general. The results also provide a basis for more fundamentally understanding the mechanisms behind conventional
antioxidants in medicine, such as ceria nanoparticles, and represent a starting point for improvement of additives that detoxify radicals or intermediates formed therefrom, e.g., via damage transfer or repair pathways.

Conflicts of interest

The authors have no conflicts of interest to disclose.

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