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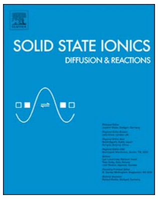

Synthesis and properties of poly(phenylene-*co*-arylene ether ketone)s with five quaternary ammonium groups on a phenyl unit for anion-exchange membranes

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ABSTRACT

A poly(phenylene-*co*-arylene ether ketone) with five quaternary ammonium (QA) groups on a phenyl unit (PQA-PPAEK) was prepared to investigate the alkaline stability of multifunctional QA groups in an anionic-exchange membrane fuel cell. The properties of the PQA-PPAEK membrane were compared with those of a polymer with the same backbone but only one quaternary ammonium group on the phenyl unit (QA-PPAEK). Due to the relatively high feeding ratio of hydrophilic to hydrophobic moieties, continuous ion clusters formed with the QA-PPAEK, which resulted in much higher hydroxide conductivities over the entire temperature range than with PQA-PPAEK. Consequently, the highest power density achieved with QA-PPAEK was 81.2 mW cm^{-2}, whereas it was 55.4 mW cm^{-2} with PQA-PPAEK. A kinetic study showed that the degradation rate of the QA groups in the locally dense PQA-PPAEK was nearly twice as high as that in QA-PPAEK, which was consistent with phenomena observed in the durability test. Moreover, the corresponding model monomer showed excellent stability under alkaline conditions, whereas PQA-PPAEK degraded much faster, with only 50% of the initial conductivity remaining after 1000 h of testing.

1. Introduction

Over the past few decades, the investigation of anion-exchange membranes (AEMs) as ion-conducting and fuel-separating materials in alkaline fuel cells has attracted considerable attention [1–3]. In view of the high-pH operation conditions, the electrochemical reaction kinetics can be strengthened, which allows the employment of non-precious electrocatalysts, promoting a remarkable reduction in the cost of fuel cells [4].

In contrast to the well-established proton-exchange membranes, which generally exhibit good chemical stability under acid conditions [5,6], the state-of-the-art AEMs are typically hampered by stability issues in basic environments. Scission of the polymer backbone (e.g., arylene ether bonds are less stable [3,7,8]) and defunctionalization of quaternary ammonium (QA) groups (e.g., by nucleophilic substitution [9,10], Hofmann elimination [11–13], or irreversible ring-opening reaction [14–16]) are considered as degradation procedures, depending on the chemical architecture. Thus, numerous efforts have been made by scientists toward improving the alkaline stability by molecular design.

Among the polymer main chains involved (e.g., poly(phenylene) oxide [17–19], poly(arylene ether ketone/sulfone)s [20–22], polystyrenes [23,24], and poly(ethylene-*co*-tetrafluoroethylene) (ETFE) [25,26]), polyphenylene derivatives display exceptionally high stability, due to the phenyl–phenyl linkages with high bond dissociation energy [27–30], and thus exhibit great potential for the construction of polymer backbones. For instance, our groups recently developed a series of poly(phenylene-*co*-arylene ether ketone)s (PPAEKs) with a mono-substituted benzyl quaternary ammonium head group [30]. The poly(arylene ether ketone) moieties with strong hydrophobicity could effectively prevent water erosion, providing good membrane robustness. In addition, all the ion-exchange groups are located in the phenylene units, and this contributes to the excellent alkaline stability.

The design strategies for stable QA groups are very challenging due to the complexity of group types, degradation mechanism, operation environments, and so forth [31,32]. In general, the scientific studies in

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recent years have been gradually focused, using chain spacers [10,33,34], steric hindrance effects [16,35,36], absence of the β-H atom [30,31], spirocyclic structures [22,31,37–39], etc. In 2015, Kreuer et al. comprehensively summarized the stability of various QA model compounds by comparing their half-time in a strong alkaline solution at 160 °C [31]. Similar to the concept put forward in this work, Jannasch and his coworkers developed side- [38] and main-chain-type [39] ionomers, both of which are based on heterocyclic QAs. The membranes, not surprisingly, showed excellent alkaline stability, even at high temperatures.

Although great progress has been achieved in recent years, it is notable that most of the degradation mechanisms were primarily studied with model compounds, typically by using an *in-situ* nuclear magnetic resonance (NMR) technology [29,31,39,40], followed by the design of monomeric or polymeric structures. However, the actual situations in the membrane, particularly in a swollen state, may not be the same or may even be considerably different, e.g., the concentration ratio of cations to anions [14,40]. The stability of monomers also does not correlate to that of the corresponding polymers under the same conditions.

Explicitly, there is a need to establish the correlation between the stability of QA groups, in both the monomer and polymer, to provide information for the design concept of an alkaline-stable polymer. Thus, we report herein the stability of QA groups in the monomer and polymers. In this study, PPAEK AEMs with pendant phenyl units with five and one QA groups were prepared to get a meaningful understanding of the structural conformation and alkaline stability. Characterizations including water uptakes, dimensional changes, hydroxide conductivities as well as a single cell performance were investigated here in detail.

2. Experimental

2.1. Materials

2,5-Dichlorobenzoyl chloride, benzoyl chloride, 1,2,3,4,5-pentamethylbenzene, 4,4′-(hexafluoroisopropylidene)diphenol, 4,4′-difluorobenzophenone, *N*-bromosuccinimide (NBS, 98%) and azodiisobutyronitrile (AIBN) were purchased from Tokyo Chemical Industry Co., Ltd. (TCI) and used as received. *N*-methyl pyrrolidone (NMP) and *N*,*N*-dimethylacetamide (DMAc) were used after dehydration over CaH_2. Bis(triphenylphosphino)nickel(II) ($Ni(PPh_3)_2Cl_2$, TCI) was initially dried at 150 °C under vacuum before use. Triphenylphosphine (PPh_3) was purchased from Sigma-Aldrich and used after recrystallization from *n*-hexane. Zinc dust (Sigma-Aldrich) was treated with 2 M HCl for 5 min, quickly filtrated, thoroughly washed with ultrapure water, ethanol, ethyl ether, successively, dried under vacuum and used immediately. Trimethylamine (ca. 45% in water) was purchased from Sigma-Aldrich and used without purification. Other reagents were used as received. Specifically, the Cl-terminated hydrophobic oligomer (**O1**) was synthesized according to our previous report [30].

2.2. Synthesis of monomers and polymers

2.2.1. Synthesis of 2,5-dichloro-2′,3′,4′,5′,6′-pentamethylbenzophenone DCPMB (M1)

Friedel-Crafts reaction was applied for the synthesis of DCPMB, using 2,5-dichlorobenzoyl chloride and 1,2,3,4,5-pentamethylbenzene in methylene chloride in the presence of $AlCl_3$ [30]. The target product was recrystallized from ethanol to form the flack-like crystals, yield: 80–85%. The ^1H and ^{13}C NMR spectra are provided in Fig. S1 in Supporting information.

FTIR (KBr, cm^{-1}): 3097, 2982 (C—H), 1680 (C=O), 1556 (C=C), 1100 (C—Cl).

^1H NMR ($CDCl_3$, ppm): Ar—H (s, 7.43), Ar—H (s, 7.41), Ar—H (m, 7.38–7.35), $-CH_3$ (s, 2.27), $-CH_3$ (s, 2.23), $-CH_3$ (s, 2.06).

^{13}C NMR ($CDCl_3$, ppm): 198.02, 137.20, 136.77, 135.60, 132.24, 131.97, 131.79, 131.01, 130.91, 128.37, 16.50, 15.93, 15.07.

2.2.2. Synthesis of PPAEK (P1)

To a 50 mL three-necked flask equipped with a nitrogen inlet and outlet, were charged with $Ni(PPh_3)_2Cl_2$ (0.066 g, 0.102 mmol), PPh_3 (0.186 g, 0.711 mmol) and zinc dust (0.265 g, 4.062 mmol). After entire exchange with nitrogen three times, 3.0 mL of anhydrous NMP was added under N_2 atmosphere and the reaction underwent a color change within 5 min (blue-yellowish brown-dark red). After that, a pre-prepared 10.0 mL NMP solution containing **M1** (0.489 g, 1.523 mmol) and **O1** (3.000 g, 0.508 mmol) was quickly added into the flask and the reaction was kept at 80 °C for 8 h under an intensively stirring. The resulting viscous mixture was cooled down to room temperature and then poured into 300 mL of 10% HCl solution. The fiber-like polymer was washed with water and methanol, collected by filtration, dried under vacuum, successively. After re-precipitation from 10 wt% of NMP to methanol, the light yellow fiber-like polymer was collected by filtration and dried under vacuum to afford a yield of 95%.

FTIR (KBr, cm^{-1}): 2870 (C—H), 1664 (C=O), 1595 (C=C), 1174 (C—O—C).

^1H NMR (DMSO-d_6, ppm): Ar—H (bm, 7.98–7.21), $-CH_3$ (bm, 2.19–1.63).

2.2.3. Synthesis of PPAEK-Br (P2)

To a 100 mL three-necked flask equipped with a nitrogen inlet and outlet, 1.000 g of **P1** and 20.0 mL of 1,1,2,2-tetrachloroethane were added. After a complete dissolution at 50 °C, NBS (0.667 g, 3.747 mmol) and AIBN (0.030 g, 0.183 mmol) were carefully added and the solution was heated to 90 °C. After the red color disappeared over 1–2 h, the solution was poured into methanol. The isolated polymer was collected by filtration, washed thoroughly with hot water and methanol, and finally dried under vacuum at 100 °C to afford a yield of 99%.

FTIR (KBr, cm^{-1}): 2870 (C—H), 1664 (C=O), 1595 (C=C), 1174 (C—O—C), 609 (C—Br).

^1H NMR (DMSO-d_6, ppm): Ar—H (bm, 7.97–7.21), $-CH_2$- (bm, 4.91–4.01).

2.2.4. Synthesis of PQA-PPAEK (P3)

To a 100 mL round-bottom flask equipped with a magnetic stirrer, 1.000 g of **P2** was dissolved into 20.0 mL of DMAc. After that, 2.0 g of 45% trimethylamine aqueous solution was slowly added. The mixture was kept stirring at room temperature for 24 h and then poured into isopropyl alcohol (IPA). The isolated polymer was collected by filtration, washed thoroughly with IPA and dried at 60 °C under vacuum to afford a yield of 85%.

FTIR (KBr, cm^{-1}): 1656 (C=O), 1594 (C=C), 1499 (C—N), 1171 (C—O—C).

^1H NMR (DMSO-d_6, ppm): Ar—H (bm, 7.97–7.21), $-CH_2$- (bs, 5.22), –QA-H (bm, 3.44–3.17).

2.2.5. Synthesis of model compound, 2,3,4,5,6-[pentakis(benzyl-N,N,N-trimethylammonium bromide) phenyl] benzophenone (PBMABB)

The detailed synthesis approaches are quite similar to those of the polymers. In particular, 2,3,4,5,6-pentamethylbenzophenone (obtained by Friedel-Crafts reaction, from benzoyl chloride and 1,2,3,4,5-pentamethylbenzene) was used as the starting material, followed by benzyl bromination, and *in-situ* amination, successively. The final product, PBMABB, was obtained with a yellow solid of an almost quantitative yield.

2,3,4,5,6-Pentamethylbenzophenone.

^1H NMR ($CDCl_3$, ppm): Ar—H (d, 7.84, 7.82), Ar—H (m, 7.56–7.53), Ar—H (m, 7.44–7.40), $-CH_3$ (s, 2.28), $-CH_3$ (s, 2.21), $-CH_3$ (s, 2.01).

2,3,4,5,6-[Pentakis(benzyl bromide) phenyl] benzophenone.