

# Synthesis of Poly(arylene ether ketone)s Bearing Skeletal Crown Ether Units for Cation Exchange Membranes

Bram Zoetebier,<sup>1</sup> Sinem Tas,<sup>2</sup> G. Julius Vancso,<sup>1</sup> Kitty Nijmeijer,<sup>2</sup> Mark A. Hempenius<sup>1</sup>

<sup>1</sup>Department of Materials Science and Technology of Polymers, Mesa<sup>+</sup> Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

<sup>2</sup>Membrane Science and Technology, Mesa<sup>+</sup> Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

Correspondence to: M. A. Hempenius (E-mail: M.A.Hempenius@utwente.nl)

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**ABSTRACT:** Poly(arylene ether ketone)s (PAEKs) are the most commonly known high-performance materials used for ion exchange and fuel cell membranes. Described here is the design of novel sulfonated PAEKs (SPAEEKs) and nonsulfonated PAEKs containing crown ether units in the main chain, which can be used in sensing applications and ion-selective membranes. To this end, 4,4'(5')-di(hydroxybenzo)-18-crown-6 was synthesized and used as monomer in a step growth polymerization to form crown ether-containing PAEKs and SPAEEKs. The successful synthesis of PAEKs containing 18-crown-6 and sulfonate groups was confirmed by gel permeation chromatography, Fourier transform infrared spectroscopy, and nuclear magnetic resonance spectroscopy. Membranes

are fabricated from the sulfonated polymers. Potassium ion transport properties of the SPAEK and crown ether-containing SPAEK membranes are assessed by diffusion dialysis. Potassium ion diffusion in the crown ether-containing SPAEK membranes is almost four times lower than K<sup>+</sup> diffusion in the native polymer membranes, without crown ether. © 2015 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* 2015, 53, 2786–2793

**KEYWORDS:** crown ether; Donnan dialysis; high performance polymers; ion exchange membranes; potassium ion transport; sulfonated poly(arylene ether ketone)s; synthesis

**INTRODUCTION** Integral membrane proteins, such as ion channels, can gate the flow of ions in and out of cells by adopting closed and open states. Controlled by different mechanisms, such as membrane potential or binding of a ligand, ion channels are of central importance for many biological functions (e.g., cell–cell communications and muscle contraction) by allowing the movement of particular ionic species across the membrane.<sup>1–3</sup> In view of the central role played by ion channels in biology, synthesis and development of artificial ion channels are of great importance for creating new functional materials. A combination of the biological ion transport mechanism with polymer chemistry has opened many avenues in materials science, particularly in sensing applications and in the area of ion-selective membranes.<sup>4–6</sup>

Crown ethers are widely used as guest molecules for ions and attract great interest in terms of mimicking the biological ion transport mechanism. These structures are able to

selectively bind specific cationic species because of the ion-dipole interaction of the positively charged metal ion with the negatively polarized oxygen atoms.<sup>7</sup> Besides their specific binding with cations, crown ethers can also function as ion carriers.<sup>8</sup> Moreover, the stacking ability of the crown ether moieties makes them a potential candidate for the design of one-dimensional ion channels.<sup>9</sup> Therefore, several interesting molecular architectures, including crown ether polymers, have been designed in the context of synthetic ion channels and responsive materials.<sup>10,11</sup>

Polymers containing crown ethers are widely used in polymer chemistry and have been around for a long time.<sup>12</sup> The first example of such a polymer, bearing crown ethers in the main chain, was published by Feigenbaum and Michel.<sup>13</sup> These authors reported a polyamide that extracted alkali cations from aqueous metal chlorides. Other polymer configurations followed soon, including end-functionalized polymers<sup>14–16</sup> or polymers with pendant crown ether groups.<sup>17</sup>

Bram Zoetebier and Sinem Tas contributed equally to this work.

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Nowadays, these crown ether-containing polymers are still intensively studied, because of their potential use in ion recognition,<sup>18,19</sup> supramolecular assemblies,<sup>20–23</sup> and self-healing gels.<sup>24–27</sup> Recent work on main chain crown ether-containing supramolecular polymers includes processing by electrospinning to form nanofibers,<sup>21</sup> polymers responsive to heat, pH, potassium cations, or competitive ligands,<sup>22,23</sup> and interesting cases where linear supramolecular polymers constructed of AB-type monomers formed supramolecular fibrils, which subsequently self-organized into cross-linked networks.<sup>24</sup> The thermo- and pH-responsive sol–gel transition of similar gels was successfully used for the controlled release of rhodamine B.<sup>25</sup> Other gels were prepared with multifunctional supramolecular monomers,<sup>26</sup> results including self-healing gels, showing 100% recovery even under 10,000% strain in less than 10 s.<sup>27</sup> Recently, fluorescent supramolecular polymers were prepared for sensing applications.<sup>28,29</sup>

Poly(arylene ether ketone)s (PAEKs) are the most commonly known high-performance materials that have been extensively studied as actuators and as ion exchange and fuel cell membranes.<sup>30–34</sup> PAEKs belong to the class of aromatic polyethers<sup>35</sup> and possess outstanding thermal stability, chemical resistance, processability, and mechanical properties.<sup>36</sup> To date, incorporation of various chemical moieties and post-modification reactions of PAEKs have been investigated.<sup>37–40</sup> However, the major current challenge in ion exchange membrane development is how to improve the selective transport of a specific ion with a very high degree of specificity. To our knowledge, there are no examples of PAEKs or even of aromatic polyethers such as poly(sulfone)s or poly(ether sulfone)s with crown ether moieties incorporated in their main chain. However, copoly(ether sulfones) of moderate molar mass containing azo linkages and crown ether units in the main chain have recently been reported.<sup>41</sup> Crown ether-containing PAEKs would alter the specific ionic selectivity and are valuable for the development of ion-selective membranes and electrodes.

Here, we report the design of novel sulfonated PAEKs (SPAEEKs) containing crown ether moieties in the main chain. The synthesized polymers were characterized by gel permeation chromatography (GPC), nuclear magnetic resonance (NMR) spectroscopy, and Fourier transform infrared (FTIR) spectroscopy, and their thermal and film-forming properties were investigated. Diffusion dialysis experiments for potassium ions were performed as a proof of concept for the use of these membranes as ion-selective materials and to elucidate the influence of crown ether moieties in the PAEK main chain on ion transport.

## EXPERIMENTAL

### Materials

Dibenzo-18-crown-6 (98%), Eaton's reagent, 4,4'-difluorobenzophenone (DFBP, 99%), bisphenol A (BPA,  $\geq 99\%$ ), 1-methyl-2-pyrrolidinone (NMP, anhydrous, 99.5%), DMSO-*d*<sub>6</sub>

(99.9 atom % D), NaOH (>98%), Na<sub>2</sub>HPO<sub>4</sub> (>99%), Na<sub>2</sub>SO<sub>3</sub> (>98%), Na<sub>2</sub>SO<sub>4</sub> (anhydrous, >99%), NaHCO<sub>3</sub> (>99.7%), and NaCl (>99%) were obtained from Sigma-Aldrich (St. Louis, MO) and used as received. K<sub>2</sub>CO<sub>3</sub> (99.9%) and *m*-chloroperbenzoic acid (77%) were also obtained from Sigma-Aldrich and dried before use. CDCl<sub>3</sub> (99.8 atom % D) was purchased from Cambridge Isotope Laboratories (Tewksbury, MA). Methanol, DMSO, THF, and dichloromethane were obtained from Biosolve, The Netherlands. Milli-Q water (Millipore, Billerica, MA) was used in all experiments. Acetone, hydrochloric acid (37%), and DMF (extra dry, 99.8%) were purchased from Acros Organics, Belgium. Glacial acetic acid was obtained from Merck (Kenilworth, NJ). Sulfonated DFBP was prepared according to a literature procedure as is described in the Supporting Information.<sup>42</sup>

### Techniques

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance III 400 MHz instrument at 400.1 and 100.6 MHz, respectively, in CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub>. <sup>1</sup>H and <sup>13</sup>C chemical shifts were based on the solvent residual signals. Peak assignments were based on <sup>1</sup>H-<sup>13</sup>C correlated 2D NMR (HSQC) spectra. FTIR spectra were measured with a Bruker ALPHA. GPC measurements were performed using a Shimadzu GPC LC-20AD equipped with a Shodex LF-801 column and a refractive index detector, using NMP-containing 0.5 mM LiBr as the eluent. GPC measurements for sulfonated polymers were carried out in NMP-containing 5 mM LiBr, using PSS GRAM analytical 30 Å and 1000 Å GPC columns and a dual detection system consisting of a differential refractometer (Waters model 410) and a differential viscometer (Viscotek model H502). Molar masses were determined relative to narrow polystyrene standards. All sample solutions were prepared at a concentration of 1 mg mL<sup>-1</sup> and filtered through a 0.45-μm PTFE filter prior to a GPC run. Thermogravimetric analysis (TGA) measurements were performed on a Perkin Elmer TGA 4000 under N<sub>2</sub> atmosphere at a linear heating rate of 20 °C min<sup>-1</sup>. Samples (10 mg) were heated over a 30–900 °C temperature range. Differential scanning calorimetry (DSC) measurements were performed on a Perkin Elmer DSC 8000. Each sample (10 mg) was subsequently cooled and heated at a rate of 20 °C min<sup>-1</sup> between 30 and 350 °C under N<sub>2</sub> atmosphere. This cycle was repeated four times. Glass transition temperatures (*T*<sub>g</sub>'s) were determined from the second heating cycle. X-ray diffraction measurements were performed using an XRD D2 Phaser Bruker instrument using Cu Kα radiation. The generator was set to 30 kV and 10 mA. Data were collected in the 2θ range of 10°–40° with an interval of 0.02°. The potassium concentration during the diffusion experiments was measured by BWB-XP flame photometer. In case of sulfonated polymers, FTIR, GPC, TGA, DSC, and XRD measurements were performed in the H-SPAEEK form.

### 4,4'(5')-Di(acetylbenzo)-18-crown-6 (1)

Dibenzo-18-crown-6 (20.0 g, 55.5 mmol), 1.5 equivalent glacial acetic acid (10.0 g, 166.5 mmol), and Eaton's reagent (145 mL) were mixed under argon.<sup>43,44</sup> The mixture was heated to 50 °C under argon and stirred overnight. About

250 g of ice was added to the cherry red mixture. The solid was filtered with a POR 3 glass filter and dissolved in 500 mL of CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with 5% aqueous NaOH solution (3 × 150 mL) and brine (150 mL). The CH<sub>2</sub>Cl<sub>2</sub> layer was dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated *in vacuo* to yield 24.71 g (99%) of product as a light yellow solid with mp 192 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 2.55 (s, 6H, CH<sub>3</sub>), 4.01–4.07 + 4.22–4.24 (m, 16H, 18C6), 6.86 (d, *J* = 8.5 Hz, 2H, Ar *o*-CH<sub>2</sub>), 7.49–7.58 (m, 4H, Ar *m*-CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 26.26 (CH<sub>3</sub>), 68.29, 69.48 (18C6), 111.02 (Ar C), 123.40 (Ar C), 130.45 (Ar C), 148.50 (Ar C–O), 152.82 (Ar C–O), 196.90 (C=O); IR: *ν* = 1666 (s, C=O), 1266 (s, C–O), and 1129 (s, C–O) cm<sup>-1</sup>.

#### 4,4'(5')-Di(acetatobenzo)-18-crown-6 (2)

To a solution of 4,4'(5')-di(acetylbenzo)-18-crown-6 (24.64 g, 55.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.5 L), dried *m*-chloroperbenzoic acid (47.35 g, 274.4 mmol) and Na<sub>2</sub>HPO<sub>4</sub> (20.7 g, 145.8 mmol) were added.<sup>43,44</sup> After the mixture was stirred for 2 days under argon atmosphere, the solution was concentrated *in vacuo*, and the organic layer was subsequently washed with 5% aqueous Na<sub>2</sub>SO<sub>3</sub> (500 mL), a saturated solution of NaHCO<sub>3</sub> (3 × 500 mL) and brine (300 mL). Then, the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated *in vacuo* to yield 23.16 g of product (86%) with mp 112 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 2.25 (s, 6H, CH<sub>3</sub>), 3.96–4.06 + 4.10–4.20 (m, 16H, 18C6), 6.60 (m, 4H, Ar *o*-CH<sub>2</sub>), 6.81 (m, 2H, Ar *m*-CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 21.18 (CH<sub>3</sub>), 68.70–69.91 (18C6), 107.36 (Ar C), 113.31 (Ar C), 113.42 (Ar C), 144.65 (Ar C–O), 146.47 (Ar C–O), 149.11 (Ar C–O), 169.83 (C=O); IR: *ν* = 1747 (s, C=O), 1202 (s, C–O), and 1123 (s, C–O) cm<sup>-1</sup>.

#### 4,4'(5')-Di(hydroxybenzo)-18-crown-6 (3)

4,4'(5')-Di(acetatobenzo)-18-crown-6 (18.9 g, 39.7 mmol) was dissolved in a mixture of CH<sub>2</sub>Cl<sub>2</sub> (725 mL) and MeOH (900 mL).<sup>43,44</sup> The mixture was purged with argon for 1 h, before adding an argon-purged solution of NaOH (6.1 g, 154 mmol) in MeOH (100 mL). The mixture was neutralized with concentrated HCl after stirring under argon for 24 h and dried *in vacuo*. The crude product was dissolved in MeOH (200 mL) and CH<sub>2</sub>Cl<sub>2</sub> (800 mL) was added. Solids were filtered off, and the filtrate was dried *in vacuo*. The product was redissolved in MeOH (100 mL) and crystallized by adding Milli-Q water (750 mL), yielding 12.8 g of pure product (82%), mp 212 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ): 3.74–3.87 + 3.91–4.04 (m, 16H, 18C6), 6.24 (dd, *J* = 2.5 and 8.5 Hz, 2H, Ar *o*-CH<sub>2</sub>), 6.39 (d, *J* = 2.5 Hz, 2H, Ar *o*-CH<sub>2</sub>), 6.72 (d, *J* = 8.5 Hz, 2H, Ar *m*-CH<sub>2</sub>), 8.97 (s, 2H, OH). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, δ): 67.5–69.4 (18C6), 101.1 (Ar *o*-C), 105.76 (Ar *o*-C), 114.15 (Ar *m*-C), 140.87 (Ar C–O), 148.94 (Ar C–O), 151.80 (C–OH); IR: *ν* = 3583 (w, OH), 1219 (s, C–O), and 1123 (s, C–O) cm<sup>-1</sup>.

#### Poly(arylene ether ketone)s (4)

A typical polycondensation was conducted as follows: A mixture of DFBP (2.18 g, 10 mmol), BPA (2.28 g, 10 mmol), and K<sub>2</sub>CO<sub>3</sub> (1.57 g, 15 mmol) was dissolved in dry NMP (16 mL)

and toluene (8 mL) in a three-necked round-bottomed flask equipped with a magnetic stirring bar, Dean-Stark trap, and thermometer. The content was heated to 150 °C for 4 h while removing water by azeotropic distillation. Heating was then continued at 175 °C for 20 h. The viscous solution was diluted with NMP, and the polymer was precipitated in a 10-fold excess of cold ethanol. The solid was filtered off and dried *in vacuo* at 60 °C. For the C-PAEKs (featuring crown ether units), part of the BPA was substituted by 4,4'(5')-di(hydroxybenzo)-18-crown-6. For the SPAEKs (featuring sulfonate units), 25 mol % of the DFBP was substituted by SDFBP. The copolymers were designated as S(*x*)-C(*y*)-PAEK, where *x* and *y* represent the mole percentages of SDFBP and di(hydroxybenzo)–18-crown-6.

#### Membrane Fabrication

S(25)-PAEK and S(25)-C(75)-PAEK 20 wt % solutions were prepared in NMP at 60 °C. The viscous solutions were cast on a glass plate with a 0.5 mm casting knife. After casting, the solvent was evaporated under N<sub>2</sub> atmosphere for 5 days at room temperature, followed by 5 days at 60 °C and 2 days at 110 °C under vacuum. Next, the membranes were peeled off from the glass plate by immersing into water and then transferred into 1.0 M HCl to convert the Na-SPAEEK into H-SPAEEK. Afterward, the membranes were rinsed several times with Milli-Q water.

#### Water Swelling

The fabricated membranes were immersed in Milli-Q water for 24 h to measure the wet weight of the membranes. Then, the wet membranes were subsequently dried at 60 °C for 24 h. Membrane swelling was calculated by the following equation:

$$\text{Swelling} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100\% \quad (1)$$

Here, *m*<sub>wet</sub> and *m*<sub>dry</sub> are the mass (g) of the wet and the dry membranes, respectively.

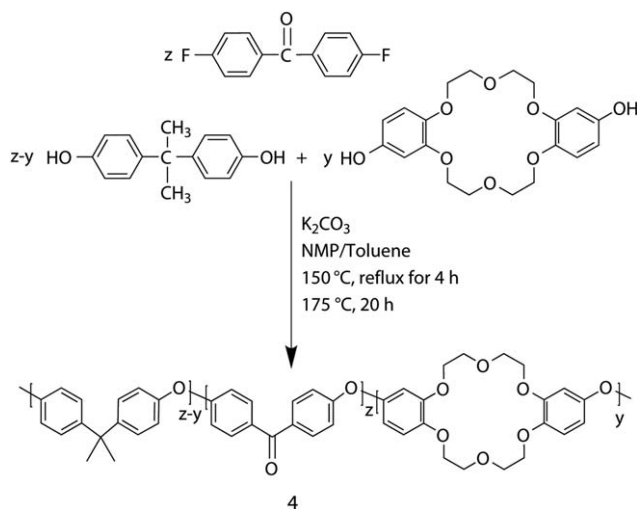
#### Permselectivity

The permselectivity of the membranes was determined by the Nernst potential method. In a two-compartment cell, KCl solutions of 0.5 M and 0.1 M are recirculated on each side of the test membrane. The membrane potential is measured by two reference electrodes. The permselectivity of the membranes was calculated by the following equation:

$$\text{permselectivity (\%)} = \frac{\Delta V_{\text{measured}}}{\Delta V_{\text{theoretical}}} \times 100\% \quad (2)$$

$$\Delta V_{\text{theoretical}} = \frac{RT}{zF} \ln \frac{C_2 \gamma_2}{C_1 \gamma_1} \quad (3)$$

Here, *R* is the gas constant (J mol<sup>-1</sup> K<sup>-1</sup>), *T* the temperature (K), *z* the electrochemical valence, *F* the Faraday constant (A s mol<sup>-1</sup>), *C*<sub>1</sub> and *C*<sub>2</sub> the concentrations of the two solutions (mol L<sup>-1</sup>), respectively, and *γ*<sub>1</sub> and *γ*<sub>2</sub> the activity coefficients of the two solutions, respectively.



**SCHEME 1** Polycondensation procedure for PAEKs bearing crown ether units in their main chain.

### Diffusion Dialysis

The two compartments of a glass diffusion cell (35 mL) were separated by the membrane under investigation with an effective area of 12 cm<sup>2</sup>. The receiver solution had a concentration of 10 mM HCl for each experiment, whereas 10 mM KCl was prepared as feed solution. Each side was constantly mixed during the diffusion experiments, and 0.1 mL samples were taken in time and analyzed using a flame photometer.

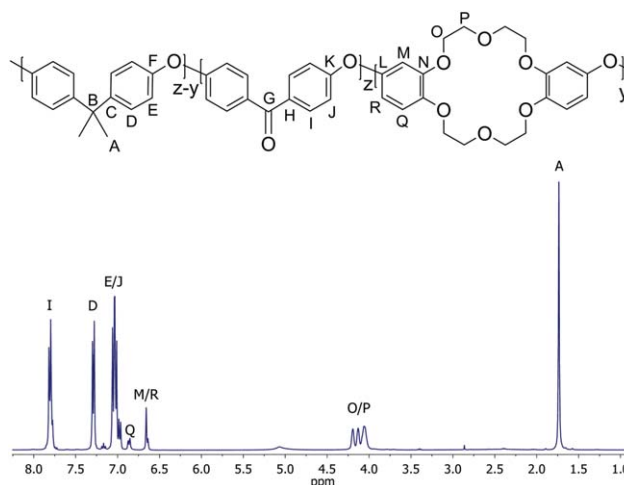
The ion flux through the membrane was calculated from the concentration change in the receiving compartment

$$J = \frac{V}{A} \frac{dc}{dt} \quad (4)$$

where  $V$  is the volume of the receiving compartment,  $A$  the membrane area, and  $dc/dt$  the concentration change in time.

### RESULTS AND DISCUSSION

In this work, we describe the direct incorporation of dibenzo-18-crown-6 units into a PAEK main chain as repeating unit. In the used step-growth polymerization, a hydroxyaryl-containing crown ether was required. Accordingly, 4,4'(5')-di(hydroxybenzo)-18-crown-6<sup>43,44</sup> **3** was synthesized (Supporting Information Scheme S1). Copolymers were synthesized by polycondensation of DFBP with BPA and 4,4'(5')-di(hydroxybenzo)-18-crown-6 at 175 °C in NMP (Scheme 1). The molar masses of the polymers were measured by GPC, and the results are summarized in Supporting Information Table S1 and Supporting Information Figure S1. The obtained polymers possessed molar masses in the range of  $M_n = 16,000$ – $33,000$  g/mol and polydispersities ranging from 1.6 to 2.9. The molar masses reached were sufficiently high to provide these polymers with useful mechanical properties, allowing the fabrication of stable membranes. The polydispersity values measured by GPC are typical of polymers prepared by step growth polymerization methods. One



**FIGURE 1** 400 MHz <sup>1</sup>H NMR spectrum of C-PAEK, recorded in CDCl<sub>3</sub>. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

exception is polymer S(25)-C(75)-PAEK ( $M_n = 29,000$  g/mol), which has a typical molar mass but a relatively high polydispersity value ( $M_w/M_n = 5.9$ ). This polymer features both crown ether units and sulfonate pendant groups, which likely interact and may influence its interactions with the stationary phase of the GPC column.

NMR studies confirmed the chemical structure of PAEK (Supporting Information Fig. S2) and C-PAEK (Fig. 1 and Supporting Information Fig. S3). The characteristic peak of the methyl groups present in the BPA units of PAEK is clearly visible in the <sup>1</sup>H NMR spectra at  $\delta = 1.74$  ppm and in the <sup>13</sup>C NMR spectra at  $\delta = 31.1$  ppm. Also, the carbonyl carbon of the DFBP units was present in the <sup>13</sup>C NMR spectra at  $\delta = 194.3$  ppm [Supporting Information Fig. S2(c)]. Furthermore, the signal associated with the hydroxy groups of BPA is missing in the spectrum of PAEK, confirming successful polymerization.

When 4,4'(5')-di(hydroxybenzo)-18-crown-6 was included in the step growth polymerization, signals of the incorporated crown ether became clearly visible. Peaks O and P (Fig. 1), <sup>1</sup>H NMR at  $\delta = 4.06$ – $4.19$  ppm belong to the protons present in the oxyethylene groups of the crown ether, whereas peaks M and Q in the <sup>1</sup>H NMR spectrum originate from the phenyl rings of the crown ether units (Fig. 1). Corresponding peaks in the <sup>13</sup>C NMR spectrum are shown in Supporting Information Figure S3. When increasing the crown ether feed ratio in the reaction mixture, the crown ether content in the polymer increased correspondingly (Supporting Information Table S1). When introducing SDFBP in the polymerization, the polymer became soluble in DMSO. In the <sup>1</sup>H NMR spectra, measured in DMSO-*d*<sub>6</sub>, new peaks emerged. Most evident is the signal associated with protons located between the sulfonate and carbonyl groups [Supporting Information Figs. S4(a) peak N and S5(b) peak B]. The signal of these protons is shifted downfield and can be used to calculate the mole percentage of

**TABLE 1** Thermal Properties of PAEKs and C-PAEKs

Polymer	$T_g^a$ (°C)	$T_5^b$ (°C)	Char Yield <sup>c</sup> (%)
PAEK	162	488	43
C(25)-PAEK	144	430	42
C(50)-PAEK	143	407	42
C(75)-PAEK	143	390	45
S(25)-PAEK	180	454	47
S(25)-C(75)-PAEK	158	285	31

<sup>a</sup> Glass transition temperature.

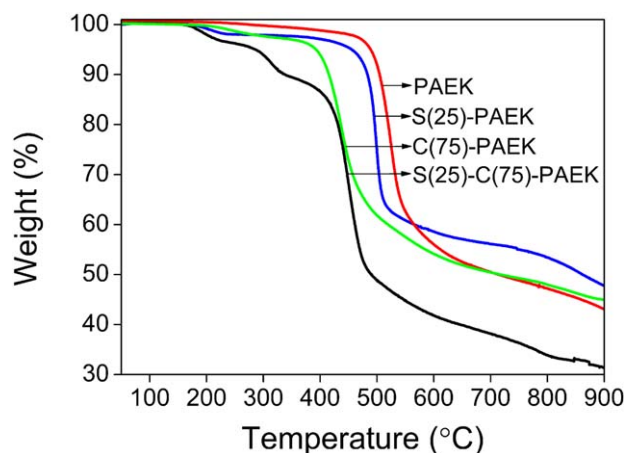
<sup>b</sup> Temperature corresponding to 5% weight loss.

<sup>c</sup> Residual mass percentage after heating to 900 °C.

sulfonated monomer introduced in the polymer chain. Combining all monomers, BPA, 4,4'(5')-di(hydroxybenzo)-18-crown-6, DFBP, and SDFBP, the NMR spectra became complex. The molar percentages were calculated with the nonoverlapping <sup>1</sup>H NMR signals (DMSO-*d*<sub>6</sub>,  $\delta$ ) 3.87+4.10 (16H), 8.33 (2H), and 1.66 (6H) corresponding to protons from the crown ether, the SDFBP, and the BPA units, respectively (Supporting Information Fig. S5).

The chemical structure of the synthesized polymers was also confirmed by FTIR. Supporting Information Figure S6 shows the FTIR spectra of PAEK, C(75)-PAEK, S(25)-PAEK, and S(25)-C(75)-PAEK. In the spectra, all polymers showed an absorbance at 1650 cm<sup>-1</sup>, which is related to the carbonyl stretching of Ar-C(=O)-Ar moieties. The typical C=C aromatic stretching bands were observed at 1590 and 1495 cm<sup>-1</sup>. The crown ether-containing polymers showed, next to the characteristic absorption bands of PAEK, also the characteristic C-O-C stretching signals of the crown ether at 1058 and 988 cm<sup>-1</sup>.<sup>45</sup> Furthermore, the absorbance values at these frequencies increased with increasing crown ether content in the polymer. This confirms the successful incorporation of dibenzo-18-crown-6 units into the polymer. Also the stretching vibration absorption of phenyl ether (C=C-O) groups at 1120 cm<sup>-1</sup> became stronger. In addition, absorption bands of the aromatic ether (Ar-O-Ar) linkages formed during polycondensation, around 1229 cm<sup>-1</sup>, were observed for all polymers synthesized. The presence of a characteristic band at 1030 cm<sup>-1</sup>, assigned to the symmetric stretching vibration of sulfonate groups, confirmed the successful introduction of these moieties in the polymer chains.<sup>46</sup>

Thermal characteristics of the synthesized polymers were determined by TGA and DSC under N<sub>2</sub> atmosphere. The results of thermogravimetric analysis, summarized in Table 1, show that crown ether incorporation influenced the thermal stability of the polymers. PAEK exhibits a high thermal stability and showed only 5% weight loss at 488 °C, whereas C(25)-PAEK, C(50)-PAEK, and C(75)-PAEK copolymers began to decompose at 430, 407, and 390 °C, respectively. C-PAEKs display a lower thermal stability because the crown ether units are more sensitive to thermal degradation than the thermally stable BPA moieties of PAEK.



**FIGURE 2** TGA curves of PAEK, C(75)-PAEK, and sulfonated copolymers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

TGA curves of the polymers are shown in Figure 2. PAEK exhibited a one-stage degradation profile, and the weight loss around 500–600 °C was assigned to intramolecular thermal cleavage of benzophenone units.<sup>47,48</sup> C(75)-PAEK copolymer also showed one weight loss step with a maximum at 414 °C, indicating that thermal decomposition was mainly due to crown ether degradation.<sup>41,49</sup> S(25)-PAEK copolymer displayed high thermal stability (5% weight loss at 454 °C), comparable with PAEK. A three-step degradation profile was observed for S(25)-C(75)-PAEK. The first weight loss at around 250 °C, typically assigned to desulfonation processes,<sup>50</sup> is followed by loss of crown ether units and decomposition of the polymer main chain. The char yield for PAEK and the C-PAEK and sulfonated copolymers remained in the 31%–47% range. The somewhat lower thermal stability of S(25)-C(75)-PAEK compared with the other C-PAEKs presented in this work, as expressed by its  $T_5$  temperature corresponding to 5% weight loss (285 °C), cannot be explained by the presence of the crown ether units, nor by the presence of the sulfonic acid pendant groups, but likely results from their combined presence in this PAEK.

The glass transition temperatures ( $T_g$ 's) were measured by DSC. As shown in Table 1, PAEK has a  $T_g$  of 162 °C, which is in good agreement with literature values.<sup>51,52</sup> PAEK has rigid arylene linkages that allow limited segmental motion, and consequently, this polymer has a relatively high  $T_g$ . However, crown ether incorporation in the polymer backbone lowered the  $T_g$  by around 20 °C for all compositions synthesized. Similar trends have been observed for crown ether-containing polyamides and polyimides.<sup>53</sup> This implies that crown ether moieties enhance chain flexibility, which may be attributed to the aliphatic ether bonds present in these macrocycles. In addition, the crown ether units likely increase free volume, which also contributes to a decrease in  $T_g$ . The introduction of sulfonate groups into PAEK and C(75)-PAEK increased the  $T_g$  by around 15 °C. Here, intermolecular ion-dipole interactions hinder the chain mobility.<sup>54</sup> No crystallization or

**TABLE 2** S(25)-PAEK and S(25)-C(75)-PAEK Membrane Properties

Membrane	$d_{\text{wet}}$ ( $\mu\text{m}$ )	Swelling (%)	Permselectivity (%)
S(25)-PAEK	$50 \pm 3$	$17 \pm 1$	$82 \pm 1$
S(25)-C(75)-PAEK	$40 \pm 5$	$22 \pm 3$	$77 \pm 2$

melting peaks were observed in the DSC traces, indicating an amorphous polymer structure.

The amorphous structure of the polymers synthesized was further confirmed by X-ray diffraction measurements. In all cases, broad amorphous scattering was observed, and crystalline reflections were completely missing.<sup>55,56</sup>

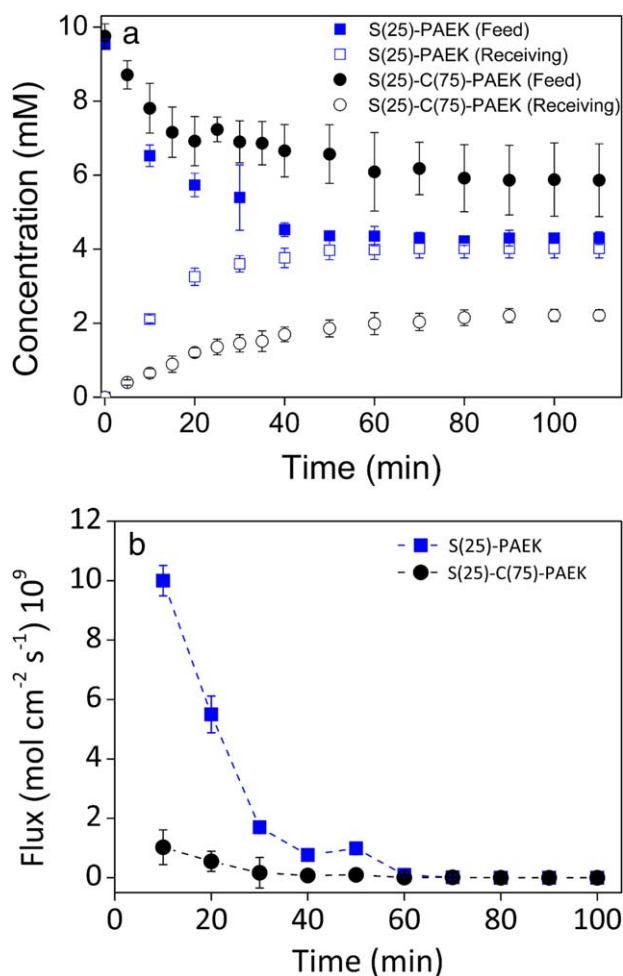
The solubility of the synthesized polymers in common organic solvents is summarized in Supporting Information Table S2. The solubility of the polymers was tested by dissolving 20 mg

of polymer in 1 mL of solvent. PAEK, C(25)-PAEK, and C(50)-PAEK showed a high solubility in polar aprotic solvents, such as NMP, DMF, and dimethylacetamide, at room temperature. These polymers also dissolved in moderately polar solvents like THF, dichloromethane, and chloroform. However, both PAEK and C(25)-PAEK were not soluble in DMSO at room temperature. PAEK, C(25)-PAEK, and C(50)-PAEK exhibited solubility in common organic solvents because of their amorphous structure. In contrast, C(75)-PAEK showed partial solubility in polar aprotic solvents as well as in moderately polar solvents. Although C(75)-PAEK also has an amorphous structure, its increased crown ether content apparently lowers the solubility of this polymer. The solubility change can be explained by stacking of crown ether units in the main chain.<sup>57,58</sup> The phenyl rings in dibenzo-18-crown-6 may favor  $\pi$ -stacking interactions.<sup>57,59</sup> The sulfonated PAEK and C-PAEK were only soluble in the aforementioned polar aprotic solvents.

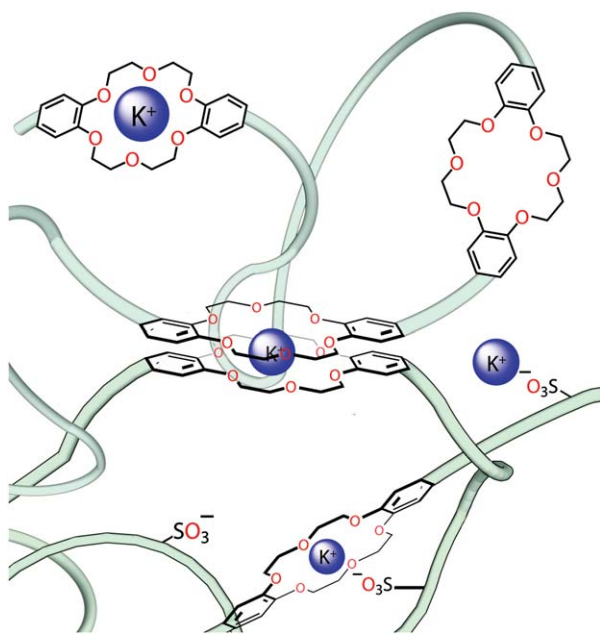
The fabricated membranes were characterized in terms of permselectivity and swelling. Membrane permselectivity is a measure of how well the membrane permits the transport of cationic species while restricting the passage of anionic ones. Membrane permselectivities are listed in Table 2. S(25)-PAEK and S(25)-C(75)-PAEK have permselectivities of around 80%. Membranes with a sulfonation degree of 65% have permselectivities of around 90%.<sup>60</sup> Membranes with low fixed charge densities (low degrees of sulfonation) exhibit low permselectivities, likely due to less effective anion exclusion.<sup>61</sup> S(25)-C(75)-PAEK had a slightly lower permselectivity compared with S(25)-PAEK. The presence of crown ether in the polymer backbone increases the counterion ( $\text{K}^+$ ) sorption in the membrane, which may reduce the effective fixed charge density. For this reason, the membrane is probably slightly less able to exclude co-ions ( $\text{Cl}^-$ ).

Water plays a critical role in ion transport within membranes. The measured water content for a S(25)-PAEK membrane was 17%. Introduction of crown ether units into the SPAEK backbone slightly increased the water content in the membrane because of the hydrophilic ether groups of the crown ether. This also contributes to a decrease in fixed charge density of the membrane.

Donnan dialysis is an ion-exchange membrane process, in which a concentration gradient over the membrane is the driving force for the transport of ions from the concentrated side of the membrane to the lower concentration side.<sup>62</sup> Potassium ion transport properties of S(25)-PAEK and S(25)-C(75)-PAEK membranes were evaluated using a two-compartment Donnan dialysis set up with the membrane under investigation positioned between the two compartments. Figure 3(a) shows the change in  $\text{K}^+$  concentration of the feed and receiving side with time for S(25)-PAEK and S(25)-C(75)-PAEK membranes. At the initial stages of the operation,  $\text{K}^+$  diffusion in the S(25)-C(75)-PAEK membrane was almost four times lower than that of the native polymer without crown ether [Fig. 3(b)]. PVA-based poly(crown ether) showed similar effects for potassium picrate, with a



**FIGURE 3** (a) Change in  $\text{K}^+$  concentration in the feed and receiving compartments for the membranes at 25 °C and (b)  $\text{K}^+$  flux through the membranes in time. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**FIGURE 4** Schematic illustration of potassium ion and S(25)-C(75)-PAEK interactions. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

twofold decrease in permeability because of strong crown ether–cation interactions.<sup>63</sup>

These results confirm the potassium-selective nature of the dibenzo-18-crown-6 in the synthesized polymer.<sup>64</sup> For nonporous membranes, diffusion of the ionic species in the membrane is the rate-limiting step, and transport of ions within the membrane is controlled by the exchange rate of ions. For the S(25)-PAEK membranes, where only sulfonate groups are present and which does not contain crown ether moieties, potassium ion transport is facilitated by a vehicle mechanism from sulfonate group to sulfonate group.<sup>65</sup> The mobility of the ions depends on the exchange kinetics between  $H^+$  and  $K^+$  ions at the sulfonate group, the swelling state of the polymer matrix, and the diffusional jump distance between the carrier (sulfonate) groups.<sup>66</sup> In addition to sulfonate–cation interactions, crown ether–cation complexation also influences the overall potassium ion transport in the S(25)-C(75)-PAEK membrane. In the synthesized crown ether polymers, the relative amount of crown ether in the membrane was kept higher than that of the  $SO_3^-$  groups, to be able to investigate the contribution of the crown ether moieties to cation transport. The dialysis results show that the presence of the crown ether units hinders the transport of  $K^+$  ions by introducing additional interactions (Fig. 4), as the crown ether is selective for  $K^+$ . The crown ether polymer can bind a  $K^+$  ion by sandwiching it between two crown ether units.<sup>63</sup> Moreover, dibenzo-18-crown-6 can form a 1:1 crown ether ring-to-cation complex with potassium ion.<sup>64</sup> Finally,  $SO_3^-$  and the crown ether can accommodate the cation together.<sup>67</sup> These interactions significantly affect the diffusion behavior of potassium ions in the S(25)-C(75)-PAEK membranes, resulting in a decrease in the transport of these ions through the membrane.

## CONCLUSIONS

A series of novel crown ether-containing PAEKs (C-PAEK)s and sulfonated C-PAEKs were successfully synthesized with reasonably high molecular weights. For this study, dihydroxy-functionalized crown ethers were used as monomer. Structural and thermal properties of the synthesized polymers were investigated. DSC and X-ray diffraction analysis confirmed that the polymers are amorphous. Membranes were fabricated from crown ether-containing sulfonated PAEKs. In Donnan dialysis, the crown ether-containing SPAEK membranes formed complexes with potassium ions, which resulted in a lower  $K^+$  diffusion compared with native sulfonated PAEK polymer films.

The idea of incorporating crown ether moieties into the SPAEK backbone could potentially be used for monovalent ion separation. Moreover, this new membrane material could inspire innovations in ion-selective electrodes and ion sensors.

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## REFERENCES AND NOTES

- 1 T. J. Jentsch, C. A. Hübner, J. C. Fuhrmann, *Nat. Cell Biol.* **2004**, *6*, 1039–1047.
- 2 N. Fertig, M. Klau, M. George, R. H. Blick, J. C. Behrends, *Appl. Phys. Lett.* **2002**, *81*, 4865–4867.
- 3 B. Hille. *Ionic Channels of Excitable Membranes*; Sinauer Verlag: Sunderland, MA, **1992**.
- 4 J. Kim, D. T. McQuade, S. K. McHugh, T. M. Swager, *Angew. Chem. Int. Ed.* **2000**, *39*, 4026–4030.
- 5 N. Schüwer, H. A. Klok, *Adv. Mater.* **2010**, *22*, 3251–3255.
- 6 J. Yin, C. H. Li, D. Wang, S. Y. Liu, *J. Phys. Chem. B* **2010**, *114*, 12213–12220.
- 7 T. J. Marrone, D. S. Hartsough, K. M. Merz, *J. Phys. Chem.* **1994**, *98*, 1341–1343.
- 8 K. Kimura, T. Sunagawa, S. Yajima, S. Miyake, M. Yokoyama, *Anal. Chem.* **1998**, *70*, 4309–4313.
- 9 B. Zhang, J. Wang, Z. Q. Yu, S. Yang, A. C. Shi, E. Q. Chen, *J. Mater. Chem. C* **2014**, *2*, 5168–5175.
- 10 N. Voyer, M. Robitaille, *J. Am. Chem. Soc.* **1995**, *117*, 6599–6600.
- 11 T. Liu, C. Y. Bao, H. Y. Wang, L. B. Fei, R. Y. Yang, Y. T. Long, L. Y. Zhu, *New J. Chem.* **2014**, *38*, 3507–3513.

- 12** Ü. Tunca, Y. Yagci, *Prog. Polym. Sci.* **1994**, *19*, 233–286.
- 13** W. M. Feigenbaum, R. H. Michel, *J. Polym. Sci., Part A: Polym. Chem.* **1971**, *9*, 817–820.
- 14** J. K. Rasmussen, H. K. Smith, *Macromol. Chem. Phys.* **1981**, *182*, 701–703.
- 15** D. M. Walba, R. M. Richards, S. P. Sherwood, R. C. Haltiwanger, *J. Am. Chem. Soc.* **1981**, *103*, 6213–6215.
- 16** R. Akashi, Y. Nagasaki, T. Tsuruta, *Macromol. Chem. Phys.* **1987**, *188*, 719–730.
- 17** T. E. Hogen-Esch, J. Smid, *J. Am. Chem. Soc.* **1972**, *94*, 9240–9241.
- 18** X. J. Ju, L. Y. Chu, P. Mi, H. Song, Y. M. Lee, *Macromol. Rapid Commun.* **2006**, *27*, 2072–2077.
- 19** A. Aydogan, D. J. Coady, S. K. Kim, A. Akar, C. W. Bielawski, M. Marquez, J. L. Sessler, *Angew. Chem. Int. Ed.* **2008**, *47*, 9648–9652.
- 20** B. Zheng, F. Wang, S. Y. Dong, F. H. Huang, *Chem. Soc. Rev.* **2012**, *41*, 1621–1636.
- 21** S. Y. Dong, L. Y. Gao, J. Z. Chen, G. C. Yu, B. Zheng, F. H. Huang, *Polym. Chem.* **2013**, *4*, 882–886.
- 22** Y. K. Tian, F. Wang, *Macromol. Rapid Commun.* **2014**, *35*, 337–343.
- 23** Y. Ding, P. Wang, Y. K. Tian, Y. J. Tian, F. Wang, *Chem. Commun.* **2013**, *49*, 5951–5953.
- 24** D. Xia, M. Xue, *Polym. Chem.* **2014**, *5*, 5591–5597.
- 25** S. Y. Dong, Y. Luo, X. Z. Yan, B. Zheng, X. Ding, Y. H. Yu, Z. Ma, Q. L. Zhao, F. H. Huang, *Angew. Chem. Int. Ed.* **2011**, *50*, 1905–1909.
- 26** Z. S. Ge, J. M. Hu, F. H. Huang, S. Y. Liu, *Angew. Chem. Int. Ed.* **2009**, *48*, 1798–1802.
- 27** M. M. Zhang, D. H. Xu, X. Z. Yan, J. Z. Chen, S. Y. Dong, B. Zheng, F. H. Huang, *Angew. Chem. Int. Ed.* **2012**, *51*, 7011–7015.
- 28** L. P. He, J. J. Liang, Y. Cong, X. Chen, W. F. Bu, *Chem. Commun.* **2014**, *50*, 10841–10844.
- 29** D. Chen, J. Y. Zhan, M. M. Zhang, J. Zhang, J. J. Tao, D. T. Tang, A. L. Shen, H. Y. Qiu, S. C. Yin, *Polym. Chem.* **2015**, *6*, 25–29.
- 30** M. Gil, X. L. Ji, X. F. Li, H. Na, J. E. Hampsey, Y. F. Lu, *J. Membr. Sci.* **2004**, *234*, 75–81.
- 31** X. Y. Shang, S. H. Tian, L. H. Kong, Y. Z. Meng, *J. Membr. Sci.* **2005**, *266*, 94–101.
- 32** J. Balster, O. Krupenko, I. Punt, D. F. Stamatialis, M. Wessling, *J. Membr. Sci.* **2005**, *263*, 137–145.
- 33** M. Tanaka, K. Fukasawa, E. Nishino, S. Yamaguchi, K. Yamada, H. Tanaka, B. Bae, K. Miyatake, M. Watanabe, *J. Am. Chem. Soc.* **2011**, *133*, 10646–10654.
- 34** J. H. Jeon, S. P. Kang, S. Lee, I. K. Oh, *Sens. Actuators B: Chem.* **2009**, *143*, 357–364.
- 35** H. R. Kricheldorf, O. Nuyken, G. Swift, *Handbook of Polymer Synthesis*; Marcel Dekker: New York, **2005**.
- 36** M. A. Hickner, H. Ghassemi, Y. S. Kim, B. R. Einsla, J. E. McGrath, *Chem. Rev.* **2004**, *104*, 4587–4611.
- 37** Z. Liu, X. B. Li, K. Z. Shen, P. J. Feng, Y. N. Zhang, X. Xu, W. Hu, Z. H. Jiang, B. J. Liu, M. D. Guiver, *J. Mater. Chem. A* **2013**, *1*, 6481–6488.
- 38** J. Miyake, M. Watanabe, K. Miyatake, *ACS Appl. Mater. Interfaces* **2013**, *5*, 5903–5907.
- 39** C. Henneuse, B. Goret, J. Marchand-Brynaert, *Polymer* **1998**, *39*, 835–844.
- 40** M. G. Dhara, S. Banerjee, *Prog. Polym. Sci.* **2010**, *35*, 1022–1077.
- 41** M. Iftime, R. Ardeleanu, N. Fifere, A. Airinei, V. Cozan, M. Bruma, *Dyes Pigments* **2014**, *106*, 111–120.
- 42** M. Ueda, H. Toyota, T. Ouchi, J. I. Sugiyama, K. Yonetake, T. Masuko, T. Teramoto, *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 853–858.
- 43** F. Wada, R. Arata, T. Goto, K. Kikukawa, T. Matsuda, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2061–2063.
- 44** J. Nam. PhD thesis. Texas Tech University: Lubbock, TX, August **1998**.
- 45** P. Diwan, S. Dollinger, K. Raetzke, A. Chandra, *Solid State Ionics* **2013**, *247*, 71–75.
- 46** P. Xing, G. P. Robertson, M. D. Guiver, S. D. Mikhailenko, K. Wang, S. Kaliaguine, *J. Membr. Sci.* **2004**, *229*, 95–106.
- 47** F. Wang, M. Hickner, Y. S. Kim, T. A. Zawodzinski, J. E. McGrath, *J. Membr. Sci.* **2002**, *197*, 231–242.
- 48** G. Montaudo, C. Puglisi, F. Samperi, *Macromol. Chem. Phys.* **1994**, *195*, 1241–1256.
- 49** C. M. F. Oliveira, *Thermochim. Acta* **1976**, *17*, 107.
- 50** W. L. Harrison, F. Wang, J. B. Mecham, V. A. Bhanu, M. Hill, Y. S. Kim, J. E. McGrath, *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2264–2276.
- 51** A. Parthiban, A. LeGuen, Y. Yansheng, U. Hoffmann, M. Klapper, K. Müllen, *Macromolecules* **1997**, *30*, 2238–2243.
- 52** A. A. Goodwin, F. W. Mercer, M. T. McKenzie, *Macromolecules* **1997**, *30*, 2767–2774.
- 53** E. M. Maya, A. E. Lozano, J. G. de la Campa, J. de Abajo, *Macromol. Rapid Commun.* **2004**, *25*, 592–597.
- 54** W. L. Harrison, M. A. Hickner, Y. S. Kim, J. E. McGrath, *Fuel Cells* **2005**, *5*, 201–212.
- 55** R. K. Krishnaswamy, D. S. Kalika, *Polymer* **1996**, *37*, 1915–1923.
- 56** D. J. Blundell, *Polymer* **1987**, *28*, 2248–2251.
- 57** E. V. Ganin, S. S. Basok, A. A. Yavolovskii, M. M. Botoshansky, M. S. Fonari, *CrystEngComm* **2011**, *13*, 674–683.
- 58** D. R. Rueda, A. Nogales, J. J. Hernandez, M. C. Garcia-Gutierrez, T. A. Ezquerro, S. V. Roth, M. G. Zolotukhin, R. Serna, *Langmuir* **2007**, *23*, 12677–12681.
- 59** C. D. Assouma, A. Crochet, Y. Cheremond, B. Giese, K. M. Fromm, *Angew. Chem. Int. Ed.* **2013**, *52*, 4682–4685.
- 60** E. Guler, R. Elizen, D. A. Vermaas, M. Saakes, K. Nijmeijer, *J. Membr. Sci.* **2013**, *446*, 266–276.
- 61** P. Dlugolecki, K. Nijmeijer, S. Metz, M. Wessling, *J. Membr. Sci.* **2008**, *319*, 214–222.
- 62** H. Strathmann. *Ion-Exchange Membrane Separation Processes*; Elsevier: Amsterdam, **2004**.
- 63** K. Kimura, M. Yoshinaga, S. Kitazawa, T. Shono, *J. Polym. Sci., Part A: Polym. Chem.* **1983**, *21*, 2777–2785.
- 64** P. D. J. Grootenhuis, P. A. Kollman, *J. Am. Chem. Soc.* **1989**, *111*, 2152–2158.
- 65** M. Saito, N. Arimura, K. Hayamizu, T. Okada, *J. Phys. Chem. B* **2004**, *108*, 16064–16070.
- 66** Y. F. Li, S. F. Wang, G. W. He, H. Wu, F. S. Pan, Z. Y. Jiang, *Chem. Soc. Rev.* **2015**, *44*, 103–118.
- 67** T. Okada, *J. Phys. Chem. B* **1998**, *102*, 3053–3059.