# Polymer Chemistry





**Cite this:** *Polym. Chem.*, 2020, **11**, 1043

Received 17th September 2019, Accepted 30th November 2019 DOI: 10.1039/c9py01403a

rsc.li/polymers

## 1. Introduction

In the present scenario, worldwide total energy consumption is too high, which is mainly attributed to an increasing population and new energy-consuming technologies. Since fossil fuels are diminishing and their burning emits a lot of greenhouse gases, alternative energy sources are being sought.<sup>1-4</sup> Among the various alternatives, proton exchange membrane (PEM) fuel cells are promising as they release water as a byproduct and use only  $H_2$  and  $O_2$  as reactants. In PEM fuel cells, the main component is the proton exchange membrane which conducts protons. Nafion® based fuel cells are the best known and most established technology which has many positive

## Polybenzimidazole co-polymers: their synthesis, morphology and high temperature fuel cell membrane properties†

Satheesh Kumar B., ២ <sup>a</sup> Balakondareddy Sana, <sup>b</sup> G. Unnikrishnan, 咆 <sup>c</sup> Tushar Jana 咆 \*<sup>b</sup> and Santhosh Kumar K. S. 咆 \*<sup>a</sup>

Polybenzimidazole (PBI) random co-polymers containing alicyclic and aromatic backbones were synthesized using two different dicarboxylic acids (viz., cyclohexane dicarboxylic acid and terephthalic acid) by varying their molar ratios. The synthesized co-polymers were characterized by inherent viscosity (IV) measurements, Fourier transform infrared spectroscopy (FTIR), <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR) spectroscopy, X-ray diffraction (XRD) and thermo-gravimetric analysis (TGA). The co-polymer composition was determined by <sup>1</sup>H NMR spectroscopy. The cyclohexyl based PBI possessed a lower proton conductivity (114 mS cm<sup>-1</sup>) than terephthalic acid based PBI (220 mS cm<sup>-1</sup>). The aromatic PBI had a high tensile modulus of 11 GPa, whereas the modulus of cyclohexyl PBI was only 2 GPa. By suitably selecting the monomer concentration, the co-polymer properties can be altered (both proton conductivity and mechanical properties). Among different co-polymers, one synthesized using 30 mol% cyclohexane dicarboxylic acid and 70 mol% terephthalic acid exhibited good elongation (8%) and modulus (10.5 GPa) values and improved proton conductivity (242 mS cm<sup>-1</sup>). In the doped condition, the co-polymer registered an elongation of 52% and a tensile modulus of 170 MPa. The high conductivity of this composition is attributed to the presence of ordered domains (shown by field emission scanning electron microscopy) present in the co-polymer in the doped condition. The co-polymers are thermally stable and the thermal stability increased with an increase in the aromatic content. Thus, alicyclic-aromatic co-polymerization is a viable technique to prepare high-temperature proton exchange membranes.

> attributes though it possesses certain drawbacks.<sup>5</sup> Low electrode kinetics, catalyst poisoning, low dimensional stability and complex water management are concerns for Nafion® based fuel cells.<sup>6-10</sup> PEMs operating at high temperature (preferably >100 °C) are highly essential to avoid these limitations (since water is the medium for proton conduction, Nafion® can operate only up to 70-80 °C).<sup>11-17</sup> As a high-temperature proton exchange membrane, phosphoric acid doped polybenzimidazole is gaining more attention due to its virtuous proton conductivity at elevated temperature, good thermal/ mechanical stability, excellent chemical resistance and no requirement for humidification.<sup>13,18-24</sup> The main challenge in PBI is to achieve both proton conductivity and the required mechanical properties in the doped condition. Generally, mechanical properties will deteriorate with an increase in the phosphoric acid doping level.<sup>20,25</sup> This may result in the breakage of the membrane inside the membrane electrode assembly.<sup>26</sup> Hence, the realization of PBI with good proton conductivity and mechanical properties is a big challenge.

> To obtain PBI with desirable properties, several attempts have been made by different groups, such as modification of the main chain,<sup>27–31</sup> the fabrication of composite



View Article Online

<sup>&</sup>lt;sup>a</sup>Polymers and Special Chemicals Division, Vikram Sarabhai Space Centre, Thiruvananthapuram-22, India. E-mail: santhoshkshankar@yahoo.com; Tel: +91471 2564661

<sup>&</sup>lt;sup>b</sup>School of Chemistry, University of Hyderabad, Hyderabad, India.

E-mail: tusharjana@uohyd.ac.in; Tel: +91-40-23134808

<sup>&</sup>lt;sup>c</sup>National Institute of Technology, Calicut, India

<sup>†</sup>Electronic supplementary information (ESI) available. See DOI: 10.1039/ c9py01403a

### Paper

membranes,<sup>32-35</sup> synthesis of cross-linked PBIs,<sup>36-39</sup> and the preparation of PBI co-polymers and blends.<sup>40-42</sup> Among the different techniques, co-polymerization has gained wide attention as the properties can be tuned by suitably selecting the monomer concentration/monomer ratio in the copolymer.<sup>43-45</sup> Zhao et al. synthesized a series of grafted polybenzimidazole co-polymers bearing polyhedral oligosilsesquioxane pendant moieties. These co-polymers exhibited mechanical properties higher than those of pristine PBI and achieved a Young's modulus of ~5 GPa and tensile strength of 85 MPa.<sup>46</sup> By coupling carboxyl functional aromatic poly (arylene ethers) with ortho diamino functional PBI oligomers, multiblock co-polymers were synthesized. Among the different co-polymers, the maximum proton conductivity obtained was only 47 mS cm<sup>-1</sup> with an acid doping of 11.5 mol RU<sup>-1</sup>. The optimized co-polymer displayed a modulus of only 2.8 GPa in the undoped condition.<sup>47</sup> Kim et al. synthesized poly (aryl ether benzimidazole) co-polymers bearing different contents of aryl ether linkages by condensation polymerization of 4,4dicarboxydiphenyl ether (DCPE) and terephthalic acid (TA) by varying the feed ratio. The tensile strength of the co-polymer with 30 mol% ether linkage was 43 MPa in the doped condition (7.5 mol H<sub>3</sub>PO<sub>4</sub>) and exhibited a proton conductivity of 98 mS cm<sup>-1</sup> at 180 °C at an acid doping level of 6.6 mol H<sub>3</sub>PO<sub>4</sub>.<sup>48</sup> A series of PBI-based block co-polymers consisting of phosphophilic PBI and phosphophobic non-PBI segments were synthesized by coupling ortho-diamino terminated m-PBI telechelic macromonomers and carboxylic acid end-capped poly(arylene ether) telechelic macromonomers. The block copolymer PBI-fluorinated poly(arylene ether), (PBI-15/fPAE-5) displayed a maximum conductivity of 108 mS cm<sup>-1</sup> with a doping of 14.6 M H<sub>3</sub>PO<sub>4</sub> with low mechanical properties (modulus ~10 MPa, tensile strength ~15 MPa) in the doped condition.<sup>49</sup> meta/para-PBI random co-polymer membranes were synthesized via phosphoric acid process. These co-polymers exhibited a good proton conductivity of 170 to 260 mS cm<sup>-1</sup> at 180 °C with an acid doping of 12 and 10 PA/PBI repeating units. However, the mechanical properties in this low doped condition were only 7 MPa (tensile strength) and 11 MPa (Young's modulus), respectively.<sup>50</sup> Segmented block copolymers of meta-PBI-block-para-PBI were synthesized with different block lengths by the reaction of diamine-terminated meta-PBI (m-PBI-Am) and acid-terminated para-PBI (p-PBI-Ac) oligomers. The reported proton conductivity for the copolymer was 110 mS cm<sup>-1</sup> at 160 °C.<sup>51</sup> Chen et al. synthesized multi-block sulfonated PBI co-polymers containing pyridine rings (sPBI40-b-PyPBI5-b-PI5). The proton conductivity of the membrane with the highest PA uptake (~200%) reached 230 S cm<sup>-1</sup> at 180 °C with a tensile strength of 87 MPa with 10% elongation.<sup>52</sup> Random co-polymers of sulfonated polyimidepolybenzimidazole (SPI-co-PBIs) were synthesized from 1,4,5,8naphthalene tetracarboxylicdianhydride, 4,4'-bis(4-aminophenoxy) biphenyl-3,3'-disulfonic acid, and an amine-terminated polybenzimidazole oligomer. The membranes featured a proton conductivity slightly higher than that of Nafion® at 100 °C with poor mechanical properties.<sup>53</sup> Co-polymers of ABPBIs containing phenoxy in the main chain were synthesized. The polymer registered a poor conductivity of ~50 mS cm<sup>-1</sup> at 160 °C and a low tensile strength of ~2 MPa in the doped condition.<sup>54</sup> Kim *et al.* prepared cross-linked copolymer membranes of benzoxazine–benzimidazole polymers and they displayed a conductivity of 120 mS cm<sup>-1</sup>.<sup>36</sup>

From the above discussion, it is very evident that the realization of co-polymers based on PBI with (i) high proton conductivity, (ii) reasonable mechanical properties in the undoped as well as doped condition and (iii) oxidative stability is very difficult. According to the literature, a *para* (phenylene) structure in the polymer backbone can give superior tensile strength, stiffness, high inherent viscosity and high conductivity.55,56 However, their elongation and oxidative stabilities are poor. By introducing an aliphatic moiety into the para (phenylene) structure, the oxidative stability and elongation of the membranes can be enhanced because aliphatic chains are less susceptible to free radical attack. In the present contribution, we have synthesized random co-polymers based on cyclohexane dicarboxylic acid and terephthalic acid (diaminobenzidine tetrahydrochloride is retained as the amine part). All the synthesized co-polymers were characterized by FTIR, XRD, TGA <sup>1</sup>H NMR, FESEM and for inherent viscosity. The proton conductivity and oxidative stability of the co-polymers were assessed. The mechanical strength of the PBI co-polymers in the undoped and acid doped conditions was evaluated. The ordering behavior of co-polymers in the doped condition is revealed in FESEM images. The swelling content and thermal properties were also studied.

## 2. Experimental

### 2.1. Materials

Diaminobenzidine tetrahydrochloride hydrate (DAB·4HCl· $xH_2O$ , 98%) and triphenyl phosphine (TPP, 99%) were received from Alfa Aesar, UK. Terephthalic acid (98%), cyclohexane-1,4-dicarboxylic acid (99%) and deuterated dimethyl sulfoxide (DMSO- $d_6$ ) were purchased from Sigma Aldrich, India. Other chemicals/ solvents such as phosphoric acid (85%), formic acid (98%) and polyphosphoric acid (8%) were purchased from Spectrochem India. Sulfuric acid (98%) was procured from Merck, India. All the chemicals were used as received without further purification.

### 2.2. Synthesis of homopolymers and co-polymers

For the synthesis of homopolymer (CHTA-0), diaminobenzidine tetra hydrochloride hydrate (4.32 g, 0.012 mmol) and terephthalic acid (1.99 g, 0.012 mmol) in the presence of triphenyl phosphine (0.2 g, 0.25 mmol) were taken in an RB containing polyphosphoric acid (90 g) under N<sub>2</sub>. The reaction mixture was heated in a programmed manner (150 °C for 3 h, 170 °C for 3 h, 190 °C for 4 h and finally at 220 °C for 13 h) to obtain a highly viscous product. It was purified by precipitation into distilled water, neutralized with sodium bicarbonate and washed with distilled water several times (5–6) and

dried in an oven at 150 °C for 24 h. In the case of homopolymer CHTA-100, the above procedure was followed by using cyclohexane-1,4-dicarboxylic acid (2.064 g, 0.012 mmol) instead of terephthalic acid. The heating programme followed was 150 °C for 3 h, 170 °C for 3 h and finally 190 °C for 5 h (the reaction stopped under this condition, because of high viscosity when further stirring was impossible). For co-polymer synthesis, the mole fraction of cyclohexane-1,4-dicarboxylic acid to terephthalic acid was varied as 1:9, 3:7, 5:5 and 9:1. For all co-polymers, the heating procedure and purification adopted were same as those of CHTA-0. Membranes were cast from the synthesized homopolymers and co-polymers by dissolving in formic acid by heating at 70 °C for 3 h and poured over a glass plate. After evaporating the formic acid by heating at 100 °C for 5 h, they were washed in boiled water and finally dried in an air oven at 150° C for 24 h. All the synthesized polymers were characterized by inherent viscosity, FTIR, XRD, TGA and <sup>1</sup>H NMR. The morphology of the membranes was studied by FESEM and the mechanical properties were studied by recording stress-strain curves. Swelling, doping and proton conductivity studies were also performed on homo/co-polymers.

## 2.3. Characterization techniques

A PerkinElmer GXA spectrophotometer with a scan rate of 4 cm<sup>-1</sup> (wave number ranging from 4000 to 400 cm<sup>-1</sup>) was used for recording Fourier transform infrared (FT-IR) spectra of homopolymers and co-polymers. The attenuated total reflectance (ATR) mode was employed for all membranes. <sup>1</sup>H NMR was recorded in a Bruker Avance IIIHD 400 MHz FTNMR spectrometer using deuterated dimethyl sulfoxide (DMSO- $d_6$ ) as solvent and TMS as the internal standard. For inherent viscosity (IV) measurements, polymers were dissolved in 98% sulfuric acid to achieve a concentration of 0.2 g dL<sup>-1</sup> at 30 °C and the measurements were made by a Cannon Ubbelohde capillary dilution viscometer F725. The X-ray diffraction patterns (XRD) of the polymers were recorded on a Bruker D8-discover X ray diffractometer with a copper anode (40 kV, 40 mA) and using Cu Kα radiation (wavelength 1.5419 Å). A solid state Lynx Eye detector with  $2\theta$  from angles 5° to 50° at a step size 0.02° in 0.5 s was used for recording the diffractograms. The crosssectional morphology of the membranes was recorded by a Carl Zeiss Ultra-55 Field Emission Scanning Electron Microscope. The dried membranes were cryo-fractured (in liquid N<sub>2</sub>) and were mounted vertically in the stub and sputter coated (with gold). The coated fractured surface was used for FESEM imaging. For measuring the proton conductivity of the membranes, a four-point-probe conductivity cell which was attached to an electrochemical impedance spectrometer Metrohm Autolab (PGSTAT302N) over a frequency range from 100 kHz to 1 Hz was used. Before measurement, the membranes were doped with phosphoric acid. For this, one set of dried membranes was taken, cut into the required dimensions of 1.5 cm × 3.0 cm and immersed in 85% phosphoric acid (CHTA-0, CHTA-10, CHTA-30 and CHTA-50) and 68% phosphoric acid (CHTA-90 and CHTA-100, because they are not stable

(completely soluble) in 85% phosphoric acid) for a period of 3 days. Lower concentrations of phosphoric acid were used in a number of previous studies.<sup>55,57,58</sup> After 3 days, the membranes were taken out, wiped with tissue paper and placed in a custom-made conductivity cell which consisted of two parallel PTFE plates. Before measurement, the presence of moisture needed to be eliminated which was done by heating the conductivity cell along with the doped membrane at 100 °C for 2 h in an oven, followed by cooling to ambient temperature. Proton conductivities at different temperatures were obtained (from impedance measurement) by means of the programmed heating of the conductivity cell along with the membrane. From the Nyquist plot, the resistance was obtained and the proton conductivity ( $\sigma$ ) was calculated as follows.

$$\sigma = \frac{L}{RA} \tag{1}$$

where  $\sigma$  is the proton conductivity (S cm<sup>-1</sup>), L is the distance (cm) between the two electrodes in the conductivity cell, A is the cross-sectional area  $(cm^2)$  of the membrane and R is the resistance  $(\Omega)$  of the membrane. To study the dimensional stability of the membranes in phosphoric acid, swelling studies were carried out according to the standard procedure (ESI 1<sup>†</sup>). To understand the stability of the membranes in an oxidative environment, oxidative stability was determined by Fenton's test (ESI 2<sup>†</sup>). To calculate the amount of phosphoric acid doped in the membranes, two similar pieces of dried membrane were taken and kept in 85 and 68% phosphoric acid for 3 days. The membranes were taken out every 24 h, surface adhered acid was removed by wiping with tissue paper and they were finally dried at 120 °C in a vacuum oven until a constant weight was obtained. From the difference in weight of the doped and dried membranes, the number of moles of phosphoric acid doped per repeating unit  $(N_{PA}/RU)$  was calculated (ESI 3<sup>†</sup>). UTM (Instron 5569 model) with a cross-head speed of 50 mm per minute under ambient conditions was used for the evaluation of tensile strength, elongation and modulus of the membranes. To study the thermal stability of the membranes, thermo-gravimetric analysis was done using TA instrument model SDT 2960 with simultaneous DTA-TGA at a heating rate of 10 °C per minute under N<sub>2</sub> atmosphere.

## 3. Results and discussion

### 3.1. Characterization of the membranes

Polybenzimidazole homopolymers based on terephthalic acid, cyclohexane dicarboxylic acid and random co-polymers based on both the acids were synthesized using the above procedure and were characterized (Schemes 1 and 2). The inherent viscosities and molecular weights of the synthesized polymers are given in Table 1. From IV, the molecular masses of all co-polymers were calculated using the Mark–Houwink equation (ESI 4†).<sup>59,60</sup> The molecular weights of the co-polymers varied between 82 and 246 kDa. Since the co-polymers are insoluble



Scheme 1 The synthesis of polybenzimidazole homo-polymers based on terephthalic acid, cyclohexane dicarboxylic acid and diaminobenzidine tetrahydrochloride. The reactions were stopped at a stage when further stirring was impossible (due to the high viscosity).



Scheme 2 The synthesis of polybenzimidazole co-polymers based on terephthalic acid, cyclohexane dicarboxylic acid and diaminobenzidine tetra hydrochloride.

Table 1	The inherent viscosities	and molecular weights o	of the synthesized	homopolymers and	l co-polymers
---------	--------------------------	-------------------------	--------------------	------------------	---------------

Dolymor	Homo-polymer		Co-polymer			
Description	CHTA-0	CHTA-100	CHTA-10	CHTA-30	CHTA-50	CHTA-90
Inherent viscosity (dL g <sup>-1</sup> ) Molecular weight (kDa)	3.46 237	1.50 082	2.74 176	2.13 128	3.56 246	3.24 218

in the common solvents used in Size Exclusion Chromatography (SEC), the average molecular weight could not be obtained by SEC.

The polymer molecular weight will have an impact on the observable properties.<sup>10</sup> It is reported that PBI membranes with a high molecular weight can show an improved mechanical property (higher stress at break) and high oxidative stability (lower degradation rate in the Fenton's test). This is attributed to an increase in polymer chain interaction with molecular weight.<sup>13,25,61</sup> High-MW PBIs possessed enhanced thermal stability compared to low molecular weight ones. High molecular weight can also increase the extent of doping and thereby increase membrane conductivity.<sup>62</sup> By increasing the

molecular weight of the membranes (from 25.0 to 36.8 kDa), an increase in tensile stress (from 3.5 to 12 MPa) was reported.<sup>13</sup> Lobato *et al.* reported that a molecular weight of 38.4 kDa displayed a stress at break of ~45 MPa, whereas the same polymer with a molecular weight of 105.1 kDa exhibited ~120 MPa.<sup>62</sup> Yang *et al.* also reported an enhancement in properties with molecular weight.<sup>63</sup>

Here, we used a lower monomer concentration (monomer: polyphosphoric acid = 2-2.5 wt%) in all the polymer syntheses to achieve a high molecular weight polymer and to overcome the lower solubility of terephthalic acid in polyphosphoric acid.<sup>45,51,64</sup> It was noted that there was an increase in inherent viscosity with terephthalic acid content in the co-polymer.

#### **Polymer Chemistry**

In the FTIR spectra of all synthesized homo and co-polymers, characteristic peaks corresponding to a benzimidazole ring were identified (Fig. 1). The peaks at 3400, 3150 and 2950 cm<sup>-1</sup> were assigned as free -N-H, self-associated -N-H and -C-H stretching, respectively. These peaks appeared in the FTIR spectra of all polymers. Also, the peaks at 1630, 1450, 1280 cm<sup>-1</sup> correspond to C=C/C=N stretching, in-plane deformation and the breathing mode of the benzimidazole ring, respectively.<sup>65–68</sup> In the co-polymers, the intensity of the peaks at 1630 and 1440 cm<sup>-1</sup> decreased with an increase in aromatic content. The peak at 1527  $\text{cm}^{-1}$  is due to in-plane ring vibration of 2-substituted benzimidazoles, which was visible only in co-polymers CHTA-100 and CHTA-90. In all other co-polymers, this peak merged with a new peak appearing at 1575 cm<sup>-1</sup>, which is ascribed to the conjugation between benzene and imidazole rings.<sup>45,64</sup> This indicates that an increase in aromatic content enhanced the conjugation between the benzene and imidazole rings. Another important observation is the broadening of the peak in the region 2500–3500 cm<sup>-1</sup> with an increase in aromatic content. In PBIs, this region corresponds to -N-H...N- hydrogen bonding. The extent of H-bonding increased with an increase in aromatic content, which resulted in peak broadening.69 All these changes indicate the presence of increased interaction in the co-polymers.

FTIR studies provide qualitative information on the copolymer structure, but a <sup>1</sup>H NMR study is more useful and was extensively used for determining the exact co-polymer composition, <sup>70–72</sup> Therefore, to find the co-polymer composition, <sup>1</sup>H NMR was recorded in deuterated dimethyl sulfoxide (DMSO- $d_6$ ) as solvent (Fig. 2). In the NMR spectrum, signals corresponding to protons of aromatic and aliphatic regions were seen and varied with respect to composition. The protons of terephthalic acid near to an imidazole ring were seen at  $\delta$ 8.4 ppm whereas the aliphatic protons of a cyclohexyl ring



Fig. 2 <sup>1</sup>H NMR spectra of the homo and co-polymers.

near to an imidazole ring were noted at 2.98, 2.27 and 1.88 ppm, respectively. The imidazole protons near to a cycloaliphatic ring appeared at 12.2 ppm whereas those near to an aromatic ring were observed at 13.2 ppm due to the shielding effect of the aromatic ring. The exact co-polymer compositions were arrived at by comparing the aliphatic/aromatic proton integrals from <sup>1</sup>H NMR (ESI 5†) and are tabulated in Table 2. Also in the NMR spectra, it was clear that the intensity of the aromatic protons increased with an increase in aromatic content and decreased for aliphatic protons.

In the powder XRD patterns of the homopolymers and copolymers, an amorphous nature was noticed similar to that of reported PBIs, except in the case of co-polymer CHTA-30 (Fig. 3). Also, it was noticed that the peak corresponding to the spacing between two parallel benzimidazole chains increased from about 19° to 26° on increasing the aromatic content.<sup>73,74</sup> The *d*-spacing decreased with an increase in the aromatic content in the co-polymer (an increase in the 2 $\theta$  value indi-



Fig. 1 FTIR spectra of the homo and co-polymers indicating changes in the spectral peaks.

Table 2 A comparison of the feed and actual monomer content values in the co-polymers based on the aromatic/aliphatic content values in the co-polymers (from  $^{1}H$  NMR)

	Feed ratio		Composition based on <sup>1</sup> HNMR <sup><i>a</i></sup> (%)		
Co-polymer	Aliphatic part	Aromatic part	Aliphatic part	Aromatic part	
CHTA-0	0	100	0	100	
CHTA-10	10	90	23	77	
CHTA-30	30	70	60	40	
CHTA-50	50	50	73	27	
CHTA-90	90	10	99	1	
CHTA-100	100	0	100	0	

<sup>a</sup> Actual compositions are corrected to two significant figures.



**Fig. 3** XRD patterns of the homo and co-polymers (arrows represent an increase in *d*-spacing with a decrease in the aromatic content).

cates a decrease in inter-planar distance) (ESI 6†). This is ascribed to enhanced interaction with an increase in aromatic content. A small peak at  $12.6^{\circ}$  can also be seen (a minor peak) which is ascribed to the length of one repeating unit.<sup>74–76</sup>

## 3.2. Morphology of the membranes

To study the morphologies of the membranes, FESEM images of the cross-section of membranes were imaged (Fig. 4). All copolymers exhibited different morphologies compared to the homopolymers. In co-polymers, a few spherical particles are clearly visible with an increase in aromatic content, which may be due to the aggregation of aromatic segments. This spherical feature is more visible in CHTA-30. An increase in conjugation in co-polymers also suggests the existence of  $\pi$ - $\pi$  interaction leading to an ordered structure (FTIR corroborates this observation).

## 3.3. Swelling and doping studies of the membranes

For swelling and doping studies, the membranes were immersed in 85 and 68% phosphoric acid for a duration of 3 days. The detailed procedure is given elsewhere (see experimental details). The results are given in Table 3.

It was noticed that the acid doping content was increased to some extent with an increase in aromatic content/inherent viscosity in the co-polymer. Aliphatic PBI exhibited a much lower doping level, whereas that of aromatic PBI was almost 3 times that of aliphatic PBI. A similar trend was also seen in the swelling volume. The high swelling volume of CHTA-50 is attributed to its high inherent viscosity. It is perceived that PA can interact with the aromatic segment much more easily than with the aliphatic part. The aliphatic structure is inefficient in creating interaction with PA or cannot hold PA in the polymer chain.

### 3.4. Proton conductivity and kinetics of proton conduction

For the measurement of proton conductivity at different temperatures, the doped membranes were placed in a custom-made four-probe conductivity cell. Then the conductivity cell along with the membrane were heated in a programmed manner from 80 °C to 160 °C and the impedance was measured using a Nyquist plot (ESI 7<sup>†</sup>). From the impedance data, proton conductivities were calculated and plotted, including error bars (Fig. 5). The conductivity measurements were made twice and the average values were reported. An error of about 2% was noted in two measurements. As expected, the conductivity increased with an increase in the quantity of doped acid and temperature. The co-polymer CHTA-30 exhibited the highest proton conductivity of 242 mS cm<sup>-1</sup> at 160 °C whereas CHTA-100 was marked by the lowest conductivity of 114 mS cm<sup>-1</sup>. The general observation is that conductivity increased with an increase in aromatic fraction. However, the homopolymer with the maximum aromatic content CHTA-0 exhibited a conductivity of 221 mS  $cm^{-1}$  (less than that of CHTA-30). Considering the quantity of acid doped, CHTA-30 contains less moles of acid (16.6) than CHTA-0 (17.5) yet its conductivity is higher than that of CHTA-0. This may be attributed to the specific ordering morphology of CHTA-30 in the presence of PA. During doping, the crystallites will absorb most of the doped acid as bonded acid, and the crystallites expand in such a way that it creates a total conduction pathway. To prove this interacting morphology, FESEM images of the doped membranes were recorded (Fig. 6). An oriented morphology and interconnection of structures are clearly visible in the FESEM of (doped) CHTA-30 which are attributed to its high conductivity. Recently Han et al. synthesized composite proton exchange membranes which exhibited improved proton conductivity due to in situ crystallization.<sup>5</sup> Beers et al. also studied the effect of crystallization on proton transport in polymer electrolyte membranes.77 To prove further the increased conductivity of CHTA-30 and the exact mechanism of proton conduction, the Arrhenius equation was used.<sup>78</sup> Arrhenius plots were drawn by plotting  $\ln(\sigma T)$  against 1/T (ESI 8<sup>†</sup>). Generally two mechanisms are used to elucidate the mechanism of proton conduction: viz., the Grotthuss and the vehicle mechanism.<sup>9,59,79,80</sup> In Arrhenius plots, a linear fit indicates proton conduction via the Grotthuss mechanism. From the figure, it can vividly be seen that the Grotthuss mechanism operates in aromatic-rich co-polymer compositions. For CHTA-90 and CHTA-100, the extent of increase in conductivity at higher temperature is less compared to that at lower temp-



Fig. 4 FESEM images of homo and co-polymers. (a) and (b) represent the homopolymers CHTA-0 and CHTA-100, (c) to (f) represent the co-polymers CHTA-10, CHTA-30, CHTA-50 and CHTA-90, respectively. Spherical features are seen in CHTA-30, which are attributed to ordered arrangements in the co-polymer.

Table 3The phosphoric acid doping and swelling volume data fromthe membranes after immersion in phosphoric acid for 3 days

Membrane	Doping $(N_{\rm PA}/\rm RU)$	Swelling volume (%)	
CHTA-0 <sup>a</sup>	17.5	296.0	
CHTA-10 <sup>a</sup>	17.7	294.0	
CHTA-30 <sup>a</sup>	16.6	300.0	
CHTA-50 <sup>a</sup>	24.5	379.0	
CHTA-90 <sup>b</sup>	6.8	79.0	
CHTA-100 <sup>b</sup>	4.7	60.2	

<sup>a</sup> Studies in 85% phosphoric acid. <sup>b</sup> Studies in 68% phosphoric acid.

erature, which resulted in deviation (linearity lost) in the Arrhenius plot at higher temperature. This may be due to the leaching of non-bonded phosphoric acid at higher temperature, so that continuous proton hopping may be interrupted.<sup>81</sup> Considering also the activation energy, CHTA-30 possessed a very low activation energy of 10.8 kJ mol<sup>-1</sup>, which also accounted for its high conductivity. In the case of CHTA-50, though it possesses a high doping content (due to high IV), it has a high activation energy (18.3 kJ mol<sup>-1</sup>) and the conduction path was tortuous (Grotthuss + vehicle) which led to low conductivity.

### 3.5. Thermal stability of membranes

The thermal stability of the membranes was studied by thermo-gravimetric analysis (TGA in N<sub>2</sub>, 10 °C per minute) (ESI 9†). The high thermal stability of all membranes is visible in the TGA profiles. With an increase in the aliphatic content in the co-polymer, thermal stability decreased due to the low thermal stability of aliphatic chains compared to rigid aromatic chains. It has been reported that breakdown of aliphatic linkages occurs at 400–600 °C.<sup>82,83</sup> Also, the char yield of the co-polymers decreased with aliphatic content. The  $T_{10\%}$  (the temperature at which 10% weight loss occurs) values of co-polymers are in the order CHTA-0 (674 °C) > CHTA-10 (642 °C) > CHTA-30 (576 °C) > CHTA-50 (530 °C) > CHTA-90 (491 °C) > CHTA-100 (480 °C).

#### 3.6. Mechanical properties of the membranes

One of the essential conditions for a membrane operating in a high-temperature fuel cell is its reasonable mechanical properties in the doped condition. The tensile properties of the co-polymers were determined by UTM (from the stress–strain curve) (Fig. 7). Table 4 details the tensile strength, elongation and modulus of all the membranes determined in undoped and doped conditions. The co-polymer CHTA-100 possesses a



Fig. 5 Proton conductivities of the homo and co-polymers at different temperatures.

low tensile modulus and high elongation. But CHTA-0 possesses a very good tensile modulus (11 GPa) with very low elongation as it contains a rigid aromatic backbone. Among the different co-polymers, CHTA-30 exhibited a very high tensile strength of 161 MPa with an elongation of 8% compared to 99 MPa and 1.9% for CHTA-0. This property enhancement during co-polymerization is attributed to the peculiar ordered morphology of CHTA-30, as seen in the FESEM images, especially in the doped condition. It was previously reported that an ordered structure can lead to enhanced proton conductivity.<sup>5,77</sup> In the case of doped membranes, the mechanical property decreases with an increase in acid doping



View Article Online

Polymer Chemistry

Fig. 7 Stress-strain curves of the homo and co-polymers under tensile conditions.

level which is due to the plasticizing effect of absorbed phosphoric acid.<sup>20,62,84,85</sup> The co-polymer CHTA-30, which possesses the highest proton conductivity, shows a reasonably good mechanical property (modulus 170 MPa, tensile strength 8 MPa and elongation 52%) after doping. The values are comparable or even better than those of several reported PBIs.<sup>25,63,86,87</sup>

### 3.7. Oxidative stability of the membranes

In a fuel cell,  $H_2O_2$  will be formed during its operation by the incomplete reduction of oxygen. This *in situ* formed  $H_2O_2$ , and the hydroxyl (HO<sup>•</sup>) and hydroperoxyl (HOO<sup>•</sup>) free radicals produced from its decomposition will attack terminal carbon-hydrogen bonds in the polymer backbone of the fuel cell



Fig. 6 FESEM images of doped co-polymer membranes reveal the changes associated with doping. (a) to (d) represent the co-polymers CHTA-10, CHTA-30, CHTA-50 and CHTA-90, respectively. An ordered nature and connectivity were observed in CHTA-30. These pockets may hold or act as reservoirs for PA.

Co-polymer	Tensile strength (MPa)		Elongation (%)		Modulus	
	Undoped	Doped	Undoped	Doped	Undoped (GPa)	Doped (MPa)
CHTA-100	64	23	27	106	2.0	227
CHTA-90	79	26	33	43	2.8	400
CHTA-50	72	13	33	229	3.0	100
CHTA-30	161	8	8	52	10.5	170
CHTA-10	99	6	3	11	8.1	270
CHTA-0	99	3	2	5	11.2	170

membrane.<sup>25,88,89</sup> As a result, the membrane undergoes oxidation and finally breakage occurs. The oxidative stability of the membranes was evaluated using Fenton's reagent. This is the commonly used test to assess the oxidative stability of the membranes, because Fenton's reagent can produce hydroxyl (HO') and hydroperoxyl (HOO') radicals and can simulate the fuel cell environment. All the homo and co-polymer membranes were immersed in Fenton's reagent at 70 °C for 120 h and the results are presented in Fig. 8. In the case of fully aromatic PBI (CHTA-0), a weight loss of 27% after 96 h of testing was observed. But for aliphatic PBI, the degradation was minimal and a weight loss of only 7.3% was recorded. The high resistance of aliphatic PBI to oxidative attack in Fenton's reagent can be explained as follows. As with the oxidative degradation mechanism proposed by different groups, attack by free radicals takes place mainly at the electron-rich centers. Due to the additional conjugation between the benzene ring of terephthalic acid and the imidazole ring, electron density is high in fully aromatic PBI (higher than in aliphatic-aromatic PBI, where terephthalic acid is replaced by cyclohexane dicarboxylic acid). Liao et al. suggested that the weak point in the polymer chain is the carbon atom linking the benzimidazole ring and the benzenoid ring.90 As hydroxyl (HO') radicals attack the carbon atom, hydrolysis of C-N/C=N bonds in the



Fig. 8 Oxidative stability of the homo and co-polymers tested for a duration of 120 h.

imidazole ring takes place, which is the reverse process to the acid-base condensation. This induces oxidation of carbon in the adjacent benzenoid ring, which eventually leads to polymer degradation. Musto et al. also studied the oxidative degradation of PBI and suggested a mechanism for the degradation.<sup>67</sup> The oxidative stability of PBI under various atmospheres was studied by Samms et al. who suggested that the weakest part of PBI through which rupture of polymer backbone takes place is the carbon in the imidazole ring linked with the phenylene group towards the amine nitrogen (-NH-).91 The increased oxidative stability of aliphatic based PBI was studied and elaborated by Bhavsar et al.92 They synthesized a series of fully aromatic and aromatic-aliphatic PBIs and observed that aromatic-aliphatic PBIs showed better oxidative stability than fully aromatic PBIs. The study proves that incorporation of -CH<sub>2</sub>- groups (aliphatic nature) via the acid moiety in PBI can enhance the oxidative stability. This is the rationale for the increased oxidative stability exhibited by aliphatic-rich composition in the present study. Considering the co-polymer membranes, oxidative stability increased with an increase in the aliphatic content. The co-polymer with the highest proton conductivity CHTA-30 exhibited a weight loss of 16.2% after 120 h of Fenton's test. The values are comparable to those for several previously reported PBI materials.<sup>63,84</sup>

In the present contribution, we have synthesized a series of PBI homopolymers and random co-polymers by varying the mol% of dicarboxylic acids used. Among the different co-polymers, the optimized composition (CHTA-30) exhibited a high proton conductivity (242 mS cm<sup>-1</sup>), good mechanical properties [tensile strength-161 MPa (undoped), 8 MPa (doped) and modulus-10.5 GPa (undoped), 170 MPa (doped)], good thermal stability ( $T_{10\%}$  – 576 °C) and enhanced oxidative stability (weight loss after 120 h of Fenton's test is 16.2%).

As described in the introduction, most reported PBI membranes have drawbacks either in terms of oxidative stability or mechanical properties (in the doped condition) or proton conductivity. Achieving these three properties together in a PBI membrane is rare.<sup>36,46–54</sup> In addition to these examples, a series of polybenzimidazole block sulfonated poly(arylene ether sulfone) *via* ring-closing condensation were synthesized by Ng *et al.*<sup>93</sup> These co-polymers exhibited a maximum conductivity of only 65 mS cm<sup>-1</sup> at 90% RH. The membranes displayed a maximum strength of 62 MPa and a modulus 2.6 GPa, respectively, in the undoped condition. Pan *et al.* synthesized a series of sulfonated polybenzimidazole–polyimide block co-polymers through condensation polymerization.<sup>94</sup> They exhibited a proton conductivity higher than 0.2 S cm<sup>-1</sup> at 160 °C, but their oxidative stability (brittle after 16 h of Fenton's test), thermal stability (degradation starts at 400 °C) and mechanical properties were poor. This discussion implies that the PBI membranes reported in this work show a significant advance in properties compared to previous PBI co-polymers of similar nature.

## 4. Conclusions

A series of polybenzimidazole random co-polymers with aliphatic and aromatic moieties were synthesized and characterized. The co-polymer composition was determined by <sup>1</sup>H NMR. The interaction between PBI chains decreased with an increase in the aliphatic content, which was indicated by an increase in *d*-spacing, as seen in the XRD patterns. One copolymer composition (CHTA-30) exhibited a more ordered structure and exhibited the highest conductivity of 242 mS cm<sup>-1</sup> at 160 °C. The ordered structure permits most of the doped acid to be in the 'bonded form', which may create a total conduction pathway that may be the rationale for the enhanced conductivity. This was evidenced in the FESEM images of the doped membranes. The mechanism of proton conduction follows the Grotthuss mechanism with a very low activation energy of 10.8 kJ mol<sup>-1</sup>. Also, the membrane exhibited good oxidative stability with weight loss of 16.2%. As a highlight, it is possible to tune the polymer backbone structure in such a way that it displays a more ordered structure, good proton conductivity, enhanced mechanical properties under doped condition and reasonably good oxidative stability by co-polymerization. Therefore, the aliphatic-aromatic PBI copolymerization route can be a versatile choice for the preparation of high-temperature fuel cell membranes.

## Conflicts of interest

There are no conflicts of interest to declare.

## Acknowledgements

The authors are grateful to the Director, VSSC for granting permission to publish this work. Analytical support from the Analytical and Spectroscopy Division is greatly acknowledged.

## References

- 1 B. C. Steele and A. Heinzel, in *Materials For Sustainable Energy: A Collection of Peer-Reviewed Research and Review Articles from Nature Publishing Group*, World Scientific, 2011, pp. 224–231.
- 2 H. Zhang and P. K. Shen, Chem. Rev., 2012, 41, 2382–2394.
- 3 J. Jagur-Grodzinski, Polym. Adv. Technol., 2007, 18, 785–799.

- 4 S. J. Peighambardoust, S. Rowshanzamir and M. Amjadi, *Int. J. Hydrogen Energy*, 2010, **35**, 9349–9384.
- 5 R. Han and P. Wu, ACS Appl. Mater. Interfaces, 2018, 10, 18351–18358.
- 6 Q. Li, R. He, J. O. Jensen and N. J. Bjerrum, *Chem. Mater.*, 2003, **15**, 4896–4915.
- 7 D. A. Notter, K. Kouravelou, T. Karachalios, M. K. Daletou and N. T. Haberland, *Energy Environ. Sci.*, 2015, **8**, 1969– 1985.
- 8 S. Subianto, Polym. Int., 2014, 63, 1134-1144.
- 9 S. S. Araya, F. Zhou, V. Liso, S. L. Sahlin, J. R. Vang, S. Thomas, X. Gao, C. Jeppesen and S. K. Kær, *Int. J. Hydrogen Energy*, 2016, 41, 21310–21344.
- L. Xiao, H. Zhang, E. Scanlon, L. Ramanathan, E.-W. Choe, D. Rogers, T. Apple and B. C. Benicewicz, *Chem. Mater.*, 2005, 17, 5328–5333.
- 11 J. A. Asensio, E. M. Sánchez and P. Gómez-Romero, *Chem. Soc. Rev.*, 2010, **39**, 3210–3239.
- 12 Q. Li, R. He, J.-A. Gao, J. O. Jensen and N. J. Bjerrum, J. Electrochem. Soc., 2003, 150, A1599–A1605.
- 13 R. He, Q. Li, A. Bach, J. O. Jensen and N. J. Bjerrum, J. Membr. Sci., 2006, 277, 38–45.
- 14 Q. Li, R. He, J. Jensen and N. Bjerrum, *Fuel Cells*, 2004, 4, 147–159.
- 15 C. Pan, R. He, Q. Li, J. O. Jensen, N. J. Bjerrum, H. A. Hjulmand and A. B. Jensen, *J. Power Sources*, 2005, 145, 392–398.
- G. Nawn, G. Pace, S. Lavina, K. Vezzù, E. Negro, F. Bertasi,
   S. Polizzi and V. Di Noto, *Macromolecules*, 2014, 48, 15–27.
- 17 E. Quartarone, S. Angioni and P. Mustarelli, *Materials*, 2017, **10**, 687.
- 18 A. Lysova, I. Stenina, A. Volkov, I. Ponomarev and A. Yaroslavtsev, *Solid State Ionics*, 2019, **329**, 25–30.
- 19 J. Wainright, J. T. Wang, D. Weng, R. Savinell and M. Litt, J. Electrochem. Soc., 1995, 142, L121–L123.
- 20 X. Li, H. Ma, H. Wang, S. Zhang, Z. Jiang, B. Liu and M. D. Guiver, RSC Adv., 2015, 5, 53870–53873.
- 21 B. P. Tripathi and V. K. Shahi, *Prog. Polym. Sci.*, 2011, 36, 945–979.
- 22 P. Kallem, A. Eguizabal, R. Mallada and M. P. Pina, ACS Appl. Mater. Interfaces, 2016, 8, 35377–35389.
- 23 I. Nicotera, V. Kosma, C. Simari, S. Angioni, P. Mustarelli and E. Quartarone, *J. Phys. Chem. C*, 2015, **119**, 9745–9753.
- 24 J. Escorihuela, A. García-Bernabé, A. Montero, A. Andrio,
  Ó. Sahuquillo, E. Gimenez and V. Compañ, *Polymers*, 2019,
  11, 1182.
- 25 Q. Li, C. Pan, J. O. Jensen, P. Noyé and N. J. Bjerrum, *Chem. Mater.*, 2007, **19**, 350–352.
- 26 M. Y. Jang and Y. Yamazaki, J. Power Sources, 2005, 139, 2-8.
- 27 J. Yang, Q. Li, L. N. Cleemann, C. Xu, J. O. Jensen, C. Pan, N. J. Bjerrum and R. He, *J. Mater. Chem.*, 2012, 22, 11185– 11195.
- 28 J. Yang, D. Aili, Q. Li, Y. Xu, P. Liu, Q. Che, J. O. Jensen, N. J. Bjerrum and R. He, *Polym. Chem.*, 2013, 4, 4768–4775.
- 29 J. Li, X. Li, Y. Zhao, W. Lu, Z. Shao and B. Yi, *ChemSusChem*, 2012, 5, 896–900.

- 30 S. Angioni, P. Righetti, E. Quartarone, E. Dilena,
  P. Mustarelli and A. Magistris, *Int. J. Hydrogen Energy*, 2011,
  36, 7174–7182.
- 31 B. Sana and T. Jana, *Polymer*, 2018, **137**, 312–323.
- 32 F. Liu, S. Wang, J. Li, X. Tian, X. Wang, H. Chen and Z. Wang, J. Membr. Sci., 2017, 541, 492–499.
- 33 G. Nawn, G. Pace, S. Lavina, K. Vezzù, E. Negro, F. Bertasi, S. Polizzi and V. Di Noto, *ChemSusChem*, 2015, 8, 1381– 1393.
- 34 B. S. Kumar, B. Sana, D. Mathew, G. Unnikrishnan, T. Jana and K. S. Kumar, *Polymer*, 2018, 145, 434–446.
- 35 B. Satheesh Kumar, B. Sana, G. Unnikrishnan, T. Jana and K. Santhosh Kumar, *J. Appl. Polym. Sci.*, 2019, 48151.
- 36 S.-K. Kim, S.-W. Choi, W. S. Jeon, J. O. Park, T. Ko, H. Chang and J.-C. Lee, *Macromolecules*, 2012, 45, 1438– 1446.
- 37 M. Hu, J. Ni, B. Zhang, S. Neelakandan and L. Wang, *J. Power Sources*, 2018, 389, 222–229.
- 38 L. Wang, Z. Liu, Y. Liu and L. Wang, J. Membr. Sci., 2019, 583, 110–117.
- 39 J. Yang, Q. Li, L. N. Cleemann, J. O. Jensen, C. Pan, N. J. Bjerrum and R. He, *Adv. Energy Mater.*, 2013, 3, 622– 630.
- 40 V. Giel, J. Kredatusová, M. Trchová, J. Brus, J. Žitka and J. Peter, *Eur. Polym. J.*, 2016, 77, 98–113.
- 41 D. Aili, I. Javakhishvili, J. Han, K. Jankova, C. Pan, S. Hvilsted, J. O. Jensen, N. J. Bjerrum and Q. Li, *Macromol. Chem. Phys.*, 2016, 217, 1161–1168.
- 42 J. Yang, Y. Xu, L. Zhou, Q. Che, R. He and Q. Li, *J. Membr. Sci.*, 2013, **446**, 318–325.
- 43 G. Qian and B. C. Benicewicz, J. Polym. Sci., Part A: Polym. Chem., 2009, 47, 4064–4073.
- 44 M. P. Kulkarni, T. J. Peckham, O. D. Thomas and S. Holdcroft, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 3654–3666.
- 45 A. Sannigrahi, D. Arunbabu, R. M. Sankar and T. Jana, *J. Phys. Chem. B*, 2007, **111**, 12124–12132.
- 46 B. Zhao, L. Cheng, Y. Bei, S. Wang, J. Cui, H. Zhu, X. Li and Q. Zhu, *Eur. Polym. J.*, 2017, 94, 99–110.
- 47 H.-S. Lee, A. Roy, O. Lane and J. E. McGrath, *Polymer*, 2008, 49, 5387–5396.
- 48 T.-H. Kim, S.-K. Kim, T.-W. Lim and J.-C. Lee, *J. Membr. Sci.*, 2008, **323**, 362–370.
- 49 F. Schönberger, G. Qian and B. C. Benicewicz, J. Polym. Sci., Part A: Polym. Chem., 2017, 55, 1831–1843.
- 50 A. T. Pingitore, F. Huang, G. Qian and B. C. Benicewicz, *ACS Appl. Mater. Interfaces*, 2019, 2, 1720–1726.
- 51 S. Maity and T. Jana, ACS Appl. Mater. Interfaces, 2014, 6, 6851–6864.
- 52 S. Chen, H. Pan, Z. Chang, M. Jin and H. Pu, *Ionics*, 2019, **25**, 2255–2265.
- 53 W. Li, X. Guo and J. Fang, *J. Mater. Sci.*, 2014, **49**, 2745–2753.
- 54 Q. Yuan, G.-H. Sun, K.-F. Han, J.-H. Yu, H. Zhu and Z.-M. Wang, *Eur. Polym. J.*, 2016, **85**, 175–186.
- 55 S. Maity and T. Jana, Macromolecules, 2013, 46, 6814-6823.

- 56 T.-H. Kim, T.-W. Lim and J.-C. Lee, *J. Power Sources*, 2007, 172, 172–179.
- 57 S. Angioni, D. C. Villa, S. Dal Barco, E. Quartarone,
  P. P. Righetti, C. Tomasi and P. Mustarelli, *J. Mater. Chem.* A, 2014, 2, 663–671.
- 58 C. He, K.-F. Han, J.-H. Yu, H. Zhu and Z.-M. Wang, *Eur. Polym. J.*, 2016, 74, 168–179.
- 59 Q. Li, J. O. Jensen, R. F. Savinell and N. J. Bjerrum, Prog. Polym. Sci., 2009, 34, 449–477.
- 60 E. Quartarone and P. Mustarelli, *Energy Environ. Sci.*, 2012, 5, 6436–6444.
- 61 J. A. Kerres, D. Xing and F. Schönberger, *J. Polym. Sci., Part B: Polym. Phys.*, 2006, 44, 2311–2326.
- 62 J. Lobato, P. Canizares, M. Rodrigo, J. Linares and J. Aguilar, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **306**, 47–55.
- 63 J. Yang, L. N. Cleemann, T. Steenberg, C. Terkelsen, Q. Li, J. O. Jensen, H. Hjuler, N. J. Bjerrum and R. He, *Fuel Cells*, 2014, 14, 7–15.
- 64 A. Sannigrahi, S. Ghosh, S. Maity and T. Jana, *Polymer*, 2010, **51**, 5929–5941.
- 65 P. Musto, F. Karasz and W. MacKnight, *Macromolecules*, 1991, 24, 4762–4769.
- 66 Q. Li, R. He, R. W. Berg, H. A. Hjuler and N. J. Bjerrum, Solid State Ionics, 2004, 168, 177–185.
- 67 P. Musto, F. Karasz and W. MacKnight, *Polymer*, 1993, 34, 2934–2945.
- 68 F. Mack, K. Aniol, C. Ellwein, J. Kerres and R. Zeis, *J. Mater. Chem. A*, 2015, 3, 10864–10874.
- 69 Y. Guan, H. Pu, M. Jin, Z. Chang and A. Modestov, *Fuel Cells*, 2012, **12**, 124–131.
- 70 J. Jouanneau, R. Mercier, L. Gonon and G. Gebel, *Macromolecules*, 2007, **40**, 983–990.
- 71 S. Qing, W. Huang and D. Yan, *Eur. Polym. J.*, 2005, **41**, 1589–1595.
- 72 Y. Li, F. Wang, J. Yang, D. Liu, A. Roy, S. Case, J. Lesko and J. E. McGrath, *Polymer*, 2006, 47, 4210–4217.
- 73 C. Xu, Y. Cao, R. Kumar, X. Wu, X. Wang and K. Scott, J. Mater. Chem., 2011, 21, 11359–11364.
- 74 A. Wereta Jr., M. T. Gehatia and D. R. Wiff, *Polym. Eng. Sci.*, 1978, 18, 204–209.
- 75 K. Scariah, V. Krishnamurthy, K. Rao and M. Srinivasan, J. Polym. Sci., Part A: Polym. Chem., 1987, 25, 2675–2687.
- 76 A. Sannigrahi, S. Ghosh, J. Lalnuntluanga and T. Jana, J. Appl. Polym. Sci., 2009, 111, 2194–2203.
- K. M. Beers, D. T. Wong, A. J. Jackson, X. Wang, J. A. Pople,A. Hexemer and N. P. Balsara, *Macromolecules*, 2014, 47, 4330–4336.
- 78 S. Singha and T. Jana, ACS Appl. Mater. Interfaces, 2014, 6, 21286–21296.
- 79 Y.-L. Ma, J. Wainright, M. Litt and R. Savinell, *J. Electrochem. Soc.*, 2004, **151**, A8–A16.
- 80 Z. Zuo, Y. Fu and A. Manthiram, *Polymers*, 2012, 4, 1627– 1644.
- 81 B. S. Kumar, B. Sana, G. Unnikrishnan, T. Jana and K. S. Kumar, *React. Funct. Polym.*, 2019, 104312.

- 82 H. Vogel and C. Marvel, J. Polym. Sci., Part A: Gen. Pap., 1961, 50, 511–539.
- 83 E. W. Neuse, in *Synthesis and Degradation Rheology and Extrusion*, Springer, 1982, pp. 1–42.
- 84 T.-H. Tang, P.-H. Su, Y.-C. Liu and T. L. Yu, *Int. J. Hydrogen Energy*, 2014, **39**, 11145–11156.
- 85 A. Y. Leykin, A. A. Askadskii, V. G. Vasilev and A. L. Rusanov, J. Membr. Sci., 2010, 347, 69–74.
- 86 J. A. Mader and B. C. Benicewicz, *Fuel Cells*, 2011, **11**, 222– 237.
- 87 J. A. Mader and B. C. Benicewicz, *Macromolecules*, 2010, 43, 6706–6715.
- 88 G. Hübner and E. Roduner, *J. Mater. Chem.*, 1999, **9**, 409–418.

- 89 A. Panchenko, H. Dilger, E. Möller, T. Sixt and E. Roduner, J. Power Sources, 2004, 127, 325–330.
- 90 J. Liao, Q. Li, H. Rudbeck, J. O. Jensen, A. Chromik, N. Bjerrum, J. Kerres and W. Xing, *Fuel Cells*, 2011, 11, 745–755.
- 91 S. Samms, S. Wasmus and R. Savinell, *J. Electrochem. Soc.*, 1996, **143**, 1225–1232.
- 92 R. S. Bhavsar, S. B. Nahire, M. S. Kale, S. G. Patil, P. P. Aher, R. A. Bhavsar and U. K. Kharul, *J. Appl. Polym. Sci.*, 2011, 120, 1090–1099.
- 93 F. Ng, B. Bae, K. Miyatake and M. Watanabe, *Chem. Commun.*, 2011, 47, 8895–8897.
- 94 H. Pan, S. Chen, M. Jin, Z. Chang and H. Pu, *Ionics*, 2018, 24, 1629–1638.