

Effect of Cation Size on Solid Polymer Electrolyte Based Dye-Sensitized Solar Cells

Bhaskar Bhattacharya,^{,†,‡} Jun Young Lee,[†] Jianxin Geng,[†] Hee-Tae Jung,[†] Jung-Ki
Park^{*,†}*

Department of Chemical and Biomolecular Engineering (BK 21 Graduate Program), Korea
Advanced Institute of Science and Technology (KAIST), 373-1 Guseong-dong, Yuseong-gu,
Daejeon, 305-701, Republic of Korea, Department of Physics, Hindustan College of Science
and Technology, Farah, Mathura – 281 122, India

Figure S1 . The DSC curves showing endothermic heat flow on melting for the polymer electrolytes. The name of the cation is mentioned for each line in the figure.

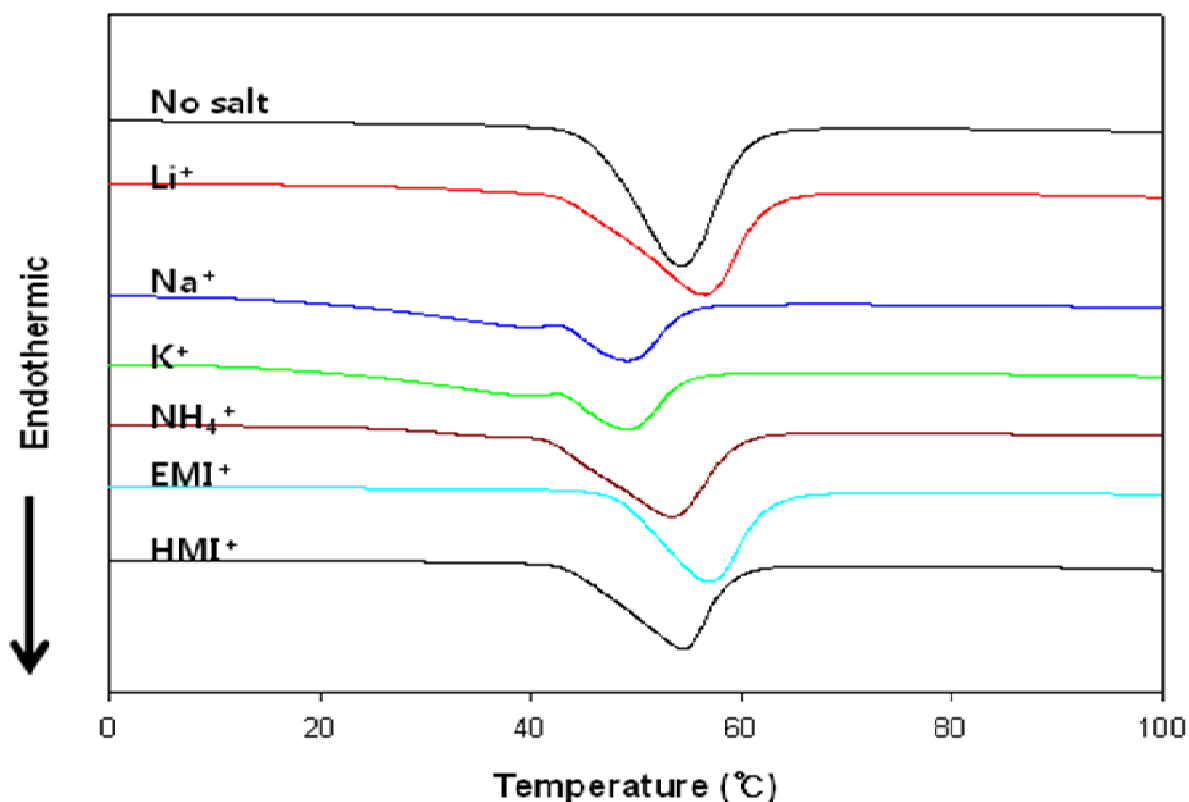
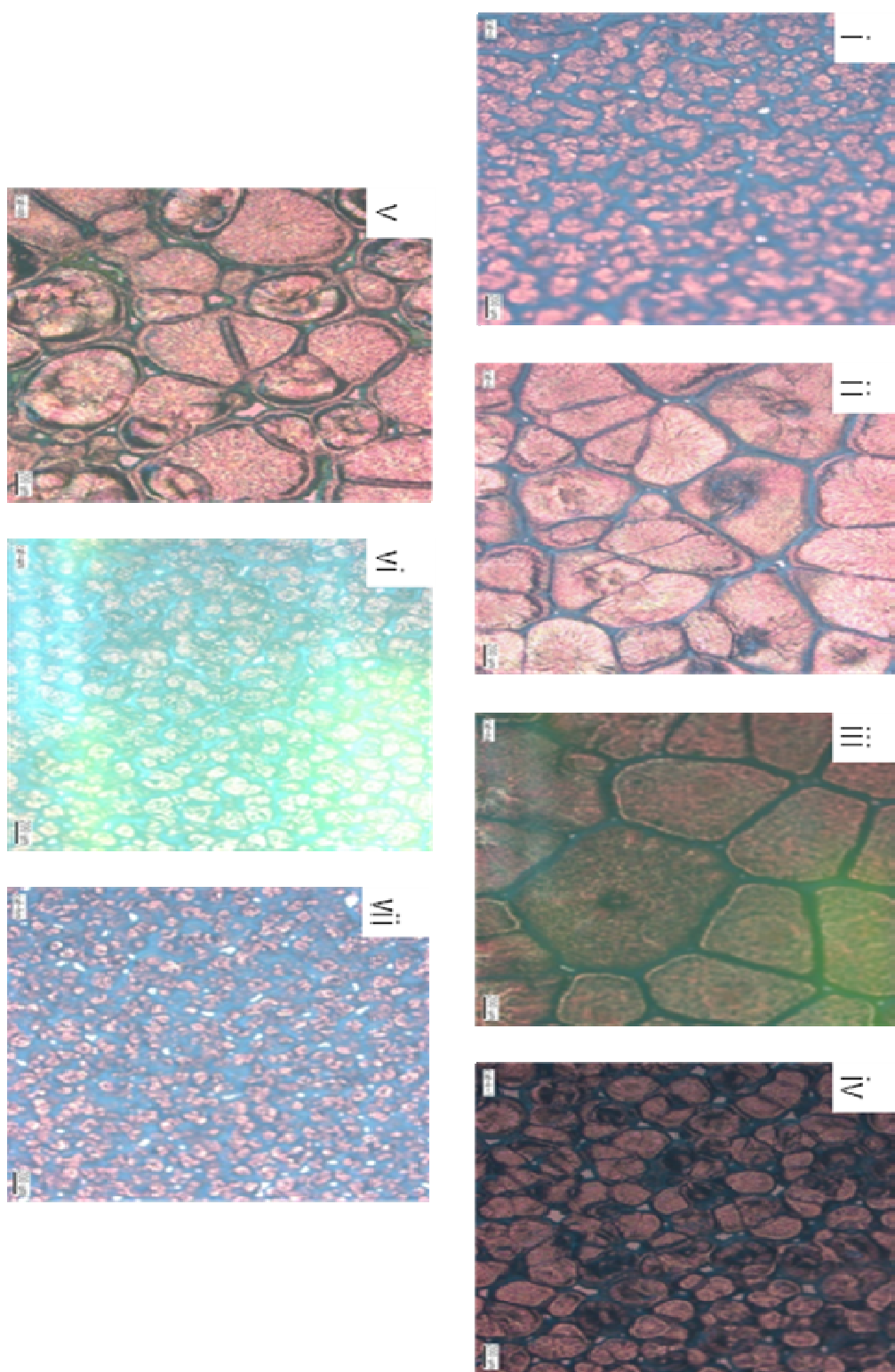


Figure 1S shows the DSC curves of the polymer electrolyte films. The melting of the crystalline part of the polymer blend and its crystalline complex with the salts could be seen. In case of the alkali and ammonium salts, two merged peaks could be seen which can be attributed to the melting of the crystalline part of the polymer-salt complex (at lower temperature) and the melting of the crystalline part of the host PEO (larger peak).

Similar observation has already been reported for the polymer-salt complexes.¹ The peak due to the crystalline complex is absent in case of the molten salt complexed polymer electrolytes which is obvious due to the amorphous (molten) nature of these salts.

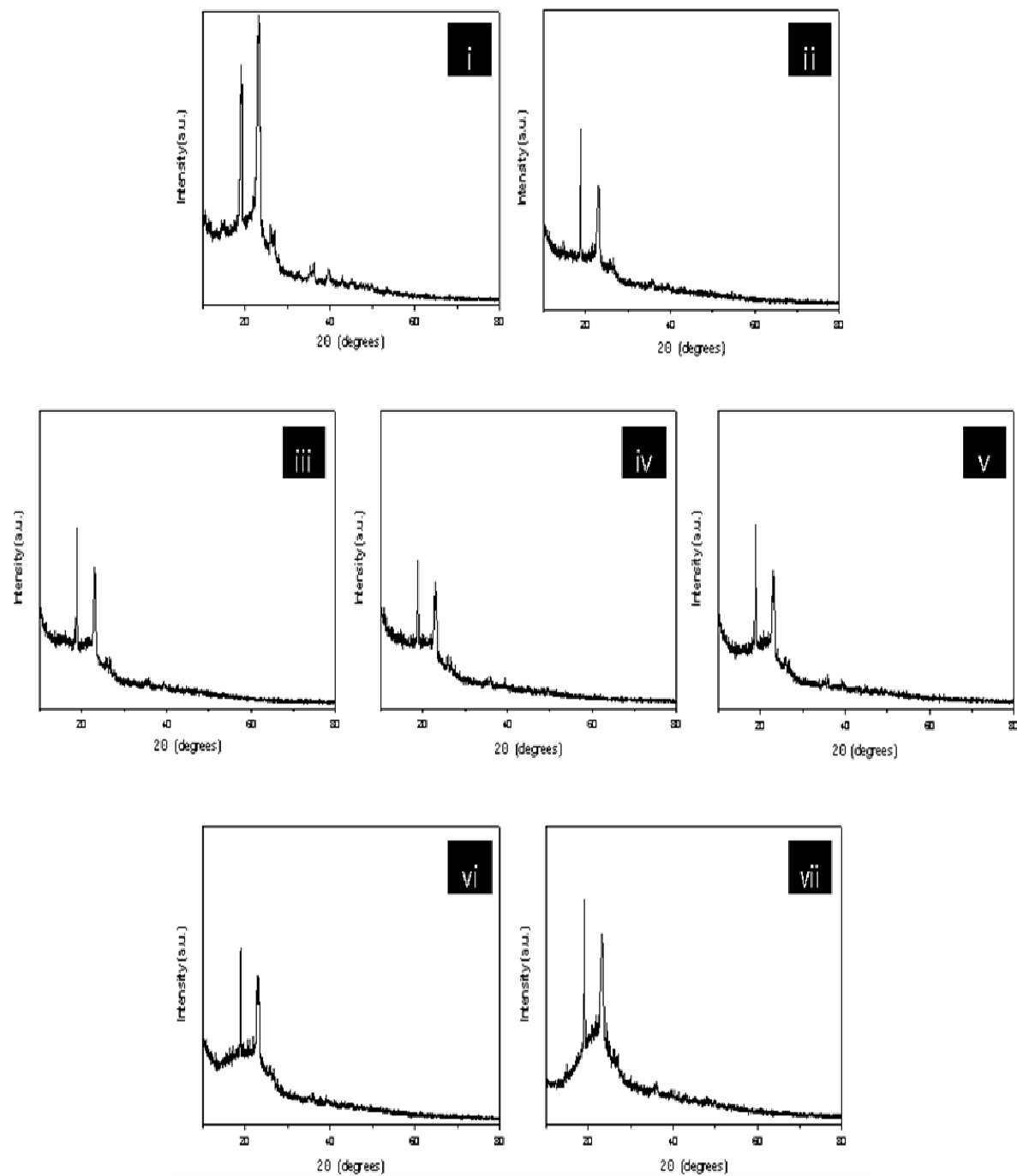
Figure S2. The polarized optical micrographs showing the spherulites and the amorphous regions (dark regions) in the PEO:PEG blend polymer films for (i) no salt, (ii) LiI, (iii) NaI, (iv) KI, (v) NH₄I, (vi) EMII, (vii)HMII



As a further confirmation to our statements, regarding the change in crystallinity, we have studied the films under polarized optical microscope. Figure S2 shows the POM images of

the films. The general feature of all the films is found to be similar. Well defined radially grown spherulitic morphology could be seen in all the films.² The dark regions between the spherulites represent the amorphous part of the polymer/polymer-salt complex is the region of our interest which is responsible for ion conduction pathway. The size of the spherulites in the film without any salt is observed to be smaller than those with the alkali and ammonium salts. This indicates that the crystallinity of the polymer increases due to salt complexation. However, this feature is not reflected in DSC measurements. A comparison between the POM photographs of our samples shows that the size of the spherulites and their density is comparable in case of the salts containing Li^+ , Na^+ and NH_4^+ but decreases for the K^+ . In other words, the crystallinity of the films with Li^+ , Na^+ and NH_4^+ appears to be comparable and it decreases for the KI complexed film. This observation, though not quantitative, is in accordance with our earlier statements made based upon the DSC measurements. In case of the EMI^+ and HMI^+ , the size of the spherulites decreases drastically and shows better amorphicity as already confirmed by the DSC. The final trend according to the size of the spherulites and in terms of the size of the cation in the films is $\text{Li}^+ \sim \text{Na}^+ \sim \text{NH}_4^+ > \text{K}^+ > \text{EMI}^+ \sim \text{HMI}^+$.

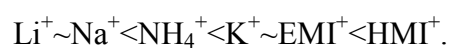
Figure S3. X-ray diffraction (XRD) of the polymer electrolytes for (i) no salt, (ii) LiI, (iii) NaI, (iv) KI, (v) NH_4I , (vi) EMII and (vii) HMII in the blend. No peaks corresponding to salts are present. The broad hump due to amorphous part of the sample is discussed in text.



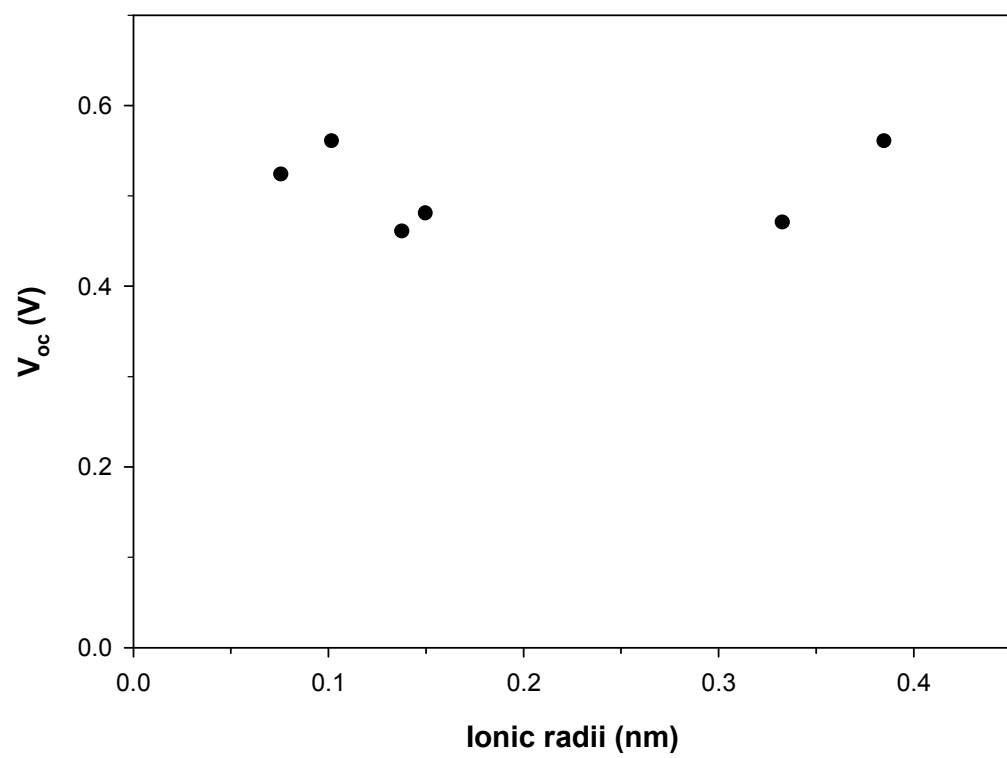
The X-ray diffraction pattern of all the films has also been obtained and shown in Figure S3. The peaks corresponding to the crystalline PEO is clearly observed in all the films. No peak corresponding to any of the iodide salts were observed which confirms our earlier

presumption that the salts get completely dissolved and complexed in the polymer matrix. The noticeable feature in these diffractograms is the broad hollow arising due to the amorphous part of the polymer. The characteristic peaks of PEO are observed riding over these hollow regions. A comparison between the area under this hump region and the intensity of the peaks due to crystalline regions indicates the change in the amorphicity of the films which is in accordance with our crystallinity measurements shown in Figure 3 in the main text.

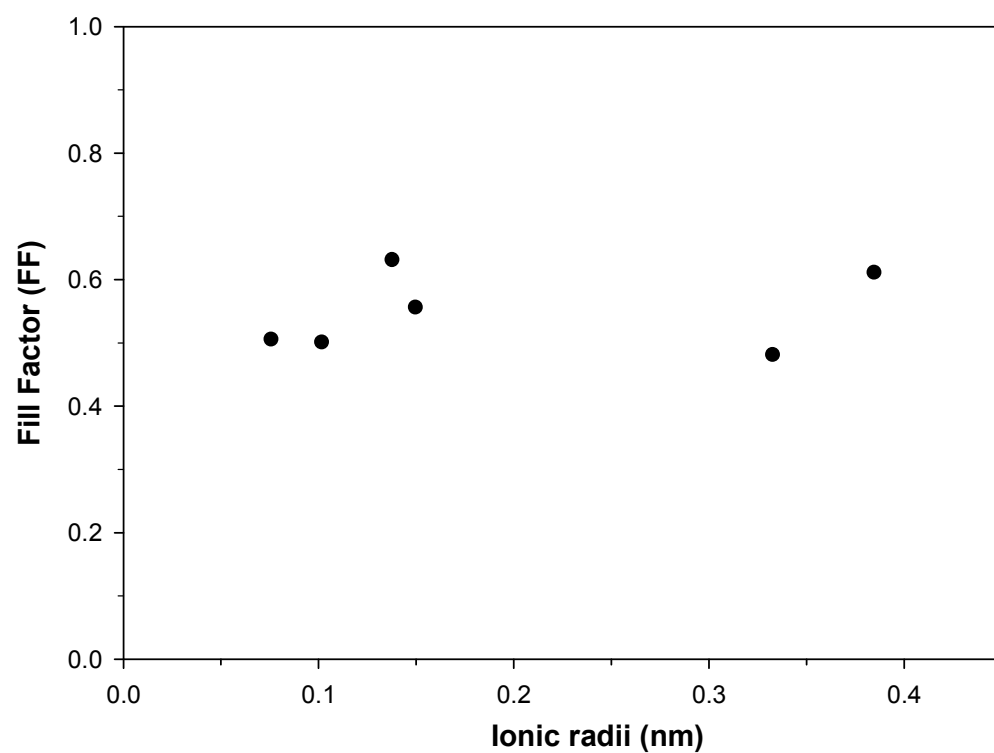
Figure S4 (a,b) : The V_{oc} and FF of the cells discussed in the paper. The V_{oc} value (Figure S4a) shows the trend $Li^+ \sim Na^+ > K^+ \sim NH_4^+ \sim EMI^+ < HMI^+$. The fill factor (Figure S4b), however, shows an increasing trend indicating better interface properties as



(a)



(b)



References

- (1) Choi, B. K. *Solid State Ionics* **2004**, 168, 123.
- (2) MacCallum, J. R.; Vincent, C. A. *Polymer electrolyte reviews* 2, Elsevier, New York, **1989**.