Supplementary information (ESI) for *Chemical Communications*

Roles of terminal groups of oligomer electrolytes in determining photovoltaic performances of dye-sensitized solar cells

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The higher chain mobility for PEGDME has been checked by differential scanning calorimetry (DSC, below Figure 1). The result shows that the T_g of PEGDME (*i.e.* -86.9 ^{o}C) is lower than that of PEG (ca. -56.8 ^{o}C). The T_g value of PEGDME is very similar to that of a reference (*i.e.* -86 ^{o}C).[1]

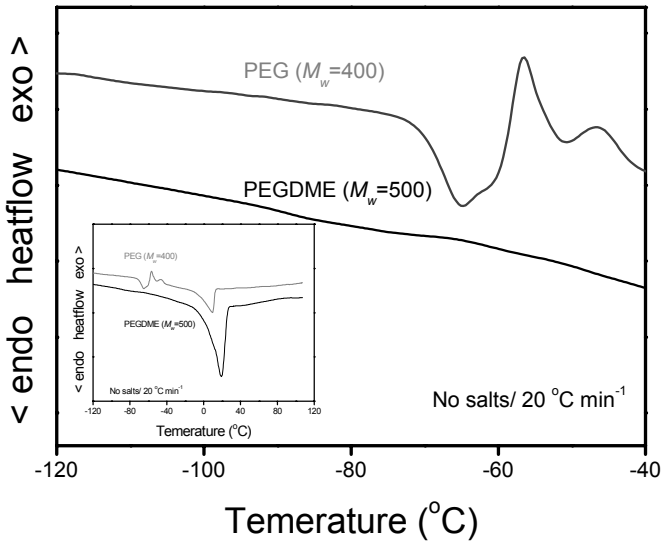

Figure 1. DSC traces for PEG (M_w=400) and PEGDME (M_w=500) in the absence of salts.

We also confirmed the hydrogen bond formation in the PEG via FT-IR spectrum (see below). First of all, the broad absorption band of O-H observed near 3450 cm^{-1} is typically assigned to the intermolecular hydrogen bonded (H-bonded) O-H stretch (cf. peak position of free O-H stretch in very dilute solution: 3650−3600 cm^{-1}).[2] Moreover, we could observe the peak shift of C-O(-C) stretching vibration (the inset of the Figure

2) to a lower wevenumber position, indicating the possibility of H-bond formation by OH-end groups of PEG.

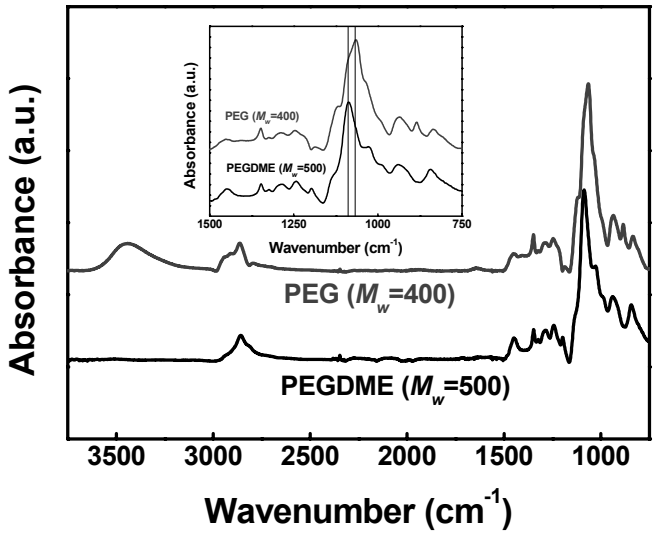

Figure 2. FT-IR spectra for PEG (M_w=400) and PEGDME (M_w=500) in the absence of salts.

It has been suggested that the steric hindrance of the methyl pendent groups along the chain limit the segmental motion required to promote ion conduction.[3] Moreover, it was suggested that this steric hindrance reduces polymer-cation interactions and can even lead to salt precipitation at elevated temperatures.[4] Figure 3 (below) shows the ion conductivities for PEO (M_w=1 M), PEO+PEGDME (M_w=500), and PEO+PPG (M_w=425) electrolytes measured with an increase of temperature. The results show that the increases in the ionic conductivities of linear PEO and PEO+oligo-PEO are more predominant than that of PEO+PPG with an elevated temperature.

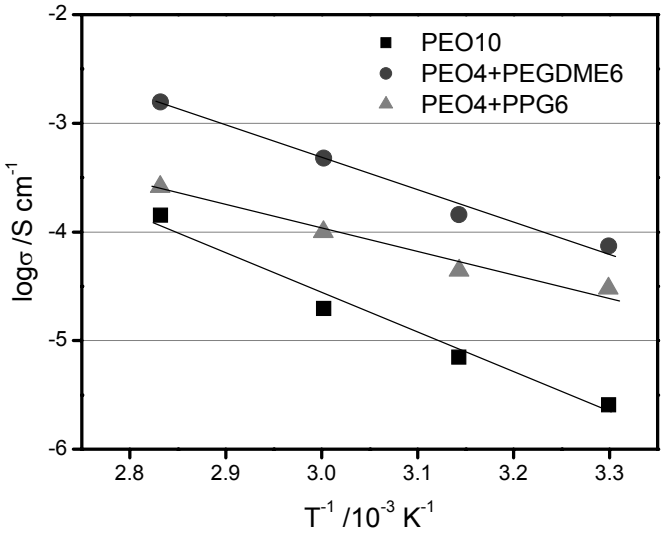

Figure 3. Ion conductivities for PEO (M_w=1 M), PEO+PEGDME (M_w=500), and PEO+PPG (M_w=425) electrolytes measured with an increase of temperature.

References:

1. M. Marcinek, M. Ciosek, G. Żukowska, W. Wieczorek, K. R. Jeffrey, J. R. Stevens, *Solid State Ionics*, 2004, **171**, 69.
2. D. L. Pavia, G. M. Lampman, G. S. Kriz, Introduction to spectroscopy: A guide for students of organic chemistry, 2nd Edition, Saunders College Publishing Co., 1996.
3. F. M. Gray, Polymer electrolytes, The Royal Society of Chemistry, Cambridge, 1997.
4. R. Frech, J. Manning, D. Teeters, B. E. Black, *Solid State Ionics*, 1988, **28-30**, 954.