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Synthesis and Characterization of a Hyper-branched Graft Polymer for Solid Polymer Electrolytes

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The ideal electrolyte material for a solvent-free solid-state battery would have both high ionic conductivity and high mechanical properties. To satisfy these rigorous performance requirements, graft copolymers of poly(methyl methacrylate-co-chloromethyl styrene) -g-poly[(oxyethylene)$_x$ methacrylate] (PMMA-g-POEM$_x$) (x=5 or 9) were synthesized by atom transfer radical polymerization (ATRP) using a copolymer poly(MMA-co-CMS) as a macroinitiator for ATRP. A solid polymer electrolyte (SPE) was prepared from the polymer obtained $LiClO_4$ and poly(ethylenglycol dimethylether)(PEG), changing PEG content in the SPE. The ionic conductivity of the SPE was 6×10^{-5} S/cm at room temperatures and the tensile strength was over 3MPa. These results indicate that SPE prepared from the hyper-branched graft copolymer has a potential application for a solid polymer electrolyte.

Key words: Solid polymer electrolyte, Ionic conductance, Mechanical strength, Atom transfer radical polymerization, Graft copolymer

1. INTRODUCTION

Solid polymer electrolytes have potential applications in many solid electrochemical devices such as solid state lithium-polymer-batteries [1-3]. The ideal solid polymer electrolyte material for these devices would not only have relatively high ionic conductivity in the solid state but also have characteristic properties such as high mechanical strength, processability and flexibility. To satisfy these rigorous performance requirements researchers have explored the design of solid electrolytes from block copolymers [4-16], which consist of covalently-bonded two chemically dissimilar polymer segments. A polymer having a high glass transition temperature (*Tg*) is chosen as one of the polymer segments because it gives high mechanical strength to SPE. The other segment should have low *Tg* and high Li salt solubility because it gives high ionic conductivity to SPE.

Block copolymers mainly have been synthesized by living anionic polymerization, which is needed for a laborious procedure that requires rigorous processes during the reaction. Hence, Mayes et al. [16] have investigated the feasibility of producing block copolymer electrolytes by atom transfer radical polymerization (ATRP) because ATRP requires little purification, and is easily scalable.

In this study, we propose a solid polymer electrolyte made from a hyper-branched graft copolymer synthesized by ATRP as one of strategies for preparation of a high performance SPE having high ionic conductivity as well as high mechanical strength. A macroinitiator of poly(MMA-co-CMS) for ATRP is prepared by copolymerization of methyl methacrylate (MMA) and chloromethylstyrene (CMS). A hyper-branched graft copolymer of PMMA-g-POEM$_x$ (x=5 or 9), which chemical structure is shown in Figure 1, is synthesized using ATRP by grafting POEM$_x$ side chains on the macro-initiator. SPEs are prepared from the polymer, $LiClO_4$ and PEG changing PEG content. The dependence of PEG content on the mechanical strength and ionic conductivity of the SPEs is investigated.

2. EXPERIMENTAL

2.1 *Synthesis of the macroinitiator for ATRP*

A macroinitiator of poly(MMA-co-CMS) for ATRP was prepared by co-polymerization of MMA and CMS by a conventional radical polymerization. The synthesis was performed as follows: Initially, as-received MMA and CMS monomers (MMA:CMS ratio = x:1 on a molar basis, x=25, 50, 100, 200) were dissolved into toluene. The system was purged for 30 min with argon, and then the initiator, 2,2'-azobisisobutyronitrile, was injected with a monomer:initiator ratio of 2000:1 on a molar basis. The synthesis was conducted at 70°C.

After the reaction, the polymer was precipitated in methanol and was dried in vacuum to constant weight.

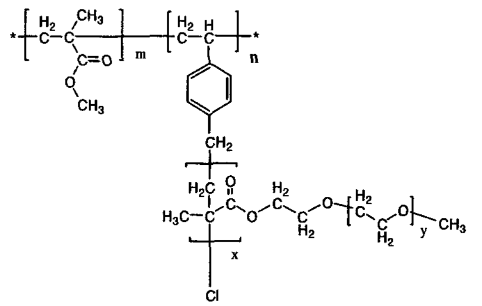

Fig. 1 Chemical structure of the hyper-branched graft copolymer synthesized in this study.

2.2. Synthesis of the hyper branch graft polymer using ATRP

The poly(MMA-co-CMS) copolymer was dissolved in 1-methyl-2-pyrrolidinone (Aldrich) solvent and poly(ethylene glycol) methyl ether methacrylate, referred to herein as poly[(oxyethylene)$_x$ methacrylate] (POEM$_x$) macromonomer was added to the solution. We used two types of POEM (POEM$_5$, *Mn*= 300g/mol: Aldrich) and (POEM$_9$, *Mn*= 475g/mol: Aldrich). The system was purged for 30 min with argon, and then copper chloride (Kanto Chem. Co. Inc.) and 4,4'-dimethyl-2,2'-dipyridyl (Aldrich) were added. The reaction was carried out at 90°C. The resulting hyper-branched graft copolymer was precipitated in petroleum ether/ethanol solvent and was dried in vacuum to constant weight.

2.3. Characterization of synthesized polymers

Gel permeation chromatography (GPC) of the macroinitiator: poly(MMA-co-CMS) was conducted at 30°C in THF at a flow rate of 1mL/min, using a HPLC pump (JASCO PU-980), GPC columns (Shodex KD-804 and KD-805) and a refractive index detector (JASCO RI-2031 plus) with an auto sampler (JASCO AS-2055 plus). The data were analyzed by a personal computer running commercially available software (System Instrument Co. 480II data station) to estimate the molecular weight and molecular weight distribution of the macroinitiators. Nuclear magnetic resonance (NMR) spectra were performed on the macroinitiators and the graft copolymers using a spectrometer for ^{1}H (JEOL JNM-EX270 FT NMR system). CDCl$_3$ was used as the solvent and tetramethylsilane as an internal standard. The data were analyzed using commercially available software (JEOL DATUM LTD. ALICE2) to estimate the CMS content in the macroinitiators and POEM content in the graft copolymers.

2.4. Preparation of solid polymer electrolyte

A solid polymer electrolyte (SPE) was made by casting a tetrafydrofuran solution of the hyper branched graft copolymers, LiClO$_4$ (Wako Pure Chemicals Ind., Ltd.) and poly(ethylenglycol dimethylether) [Mn=250, PEG, MERCK] on Teflon sheet and by drying it at 30°C for 24h. Li$^+$:[EO] ratio in all the SPEs is 1:10.

2.5 Measurement of ionic conductivity of the SPE

The SPE was punched out as a 10mm diameter of a round shape sheet using a punch. The electrical conductivity at 23°C was determined by impedance spectroscopy using a chemical impedance meter (HIOKI 3532-80) controlled by a personal computer.

2.6 Measurement of mechanical strength of the SPE

The mechanical strength of the SPEs was determined with a table model-testing machine (SHIMAZU, EZ-Test500N). In the static stress-strain curves, specimens with a nominal 20-mm-gauge length and 0.2-mm thickness were deformed in tension at a constant strain rate of 10mm/min at 25°C, and stress-strain data were determined to failure.

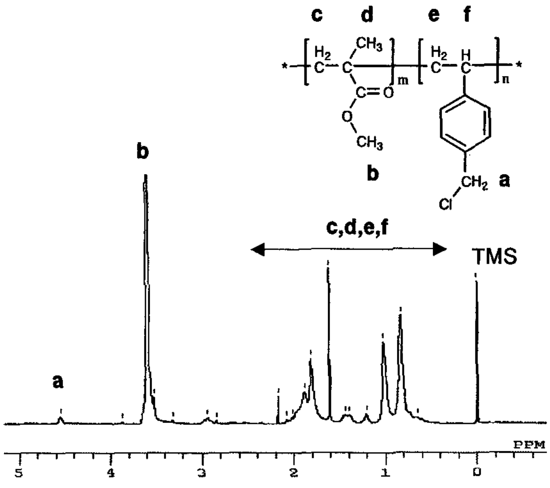

Fig. 2 ^{1}H NMR spectra in CDH$_3$ of one of the poly(MMA-co-CMS) copolymer (the macroinitiator), where MMA/CMS ratio=80:1 in the copolymer.

3. RESULTS AND DISCUSSION

3.1 Characterization of the macroinitiator

We synthesized a copolymer of poly(MMA-co -CMS) as a macroinitiator of ATRP changing their MMA/CMS composition. The NMR spectrum of one of the copolymers shown in Figure 2 has signals at 3.6 and 4.5 ppm corresponding to the methoxy group of the PMMA segment and the benzyl chloride groups, respectively. We calculated CMS composition in the macroinitiator using the ratio of the integrated areas of the methoxy group to that of the benzyl chloride groups. Figure 3 shows the relationship between the CMS composition in feed and that in the macroinitiators calculated from the NMR data. The CMS composition in the macroinitiators has a good correlation with CMS composition in feed. This means that the average length in the proposed structure of the graft copolymer can be controlled by changing the MMA/CMS ratio in the copolymerization of the macroinitiator. The GPC data show that the molecular weight and molecular weight distribution of the macroinitiators are Mn=99000 and Mw/Mn=2.12, respectively.

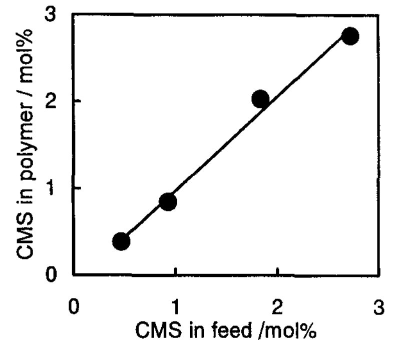

Fig. 3 The relationship between the CMS composition in feed and that in the macroinitiators calculated from the NMR data.

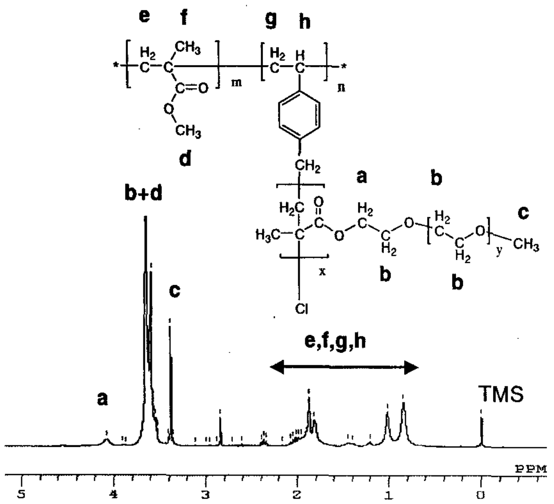

Fig. 4 ^1H NMR spectra in CDH_3 of one of the hyper-branched graft copolymers. $POEM_5$ content in the graft polymer is 28wt%.

3.2 Characterization of the hyper-branched graft polymer

The copolymers contain functional benzyl chloride groups, which are able to initiate the ATRP of POEM. The ^1H NMR spectroscopic analysis of one of the hyper branched graft-polymer shown in Figure 4 confirms the proposed structure of the graft copolymer: Grafting of POEM to the poly(MMA-co-CMS) macroinitiator resulted in the appearance of peaks in the region of 3.2-4.3 ppm due to the O-CH_x bonding environments in the methacrylate and PEO moieties of POEM [16]. We calculated POEM composition in the graft copolymer using the ratio of the integrated areas of the methoxy group to that of PEO moieties of POEM. In the ^1H NMR spectra of the graft copolymer, the signal at 4.5 ppm corresponding to the initial benzyl chloride groups of the macroinitiators disappeared. Therefore, it is assumed that the efficiency of the macroinitiator was close to 100%.

3.3 Mechanical strength of the SPEs prepared from the hyper-branched graft polymer

Solid polymer electrolytes (SPEs) were made from the hyper branched graft-polymers containing $POEM_5$ or $POEM_9$, $LiClO_4$ and poly ethylene glycol dimethylether (PEG), changing PEG content. Figure 5 shows the tensile strength and Young's modulus of the SPEs using the $POEM_5$ graft-polymer as a function of PEG content. Both the tensile strength and Young's modulus decrease with increasing PEG content. The SPE containing 28wt% of PEG has 2Mpa of tensile strength. The mechanical strength of the SPE prepared from the $POEM_9$ graft-polymer, whose data are not shown here, has almost same values as that from the $POEM_5$ graft-polymer. These results indicate that the SPEs have enough mechanical strength for solid state polymer batteries.

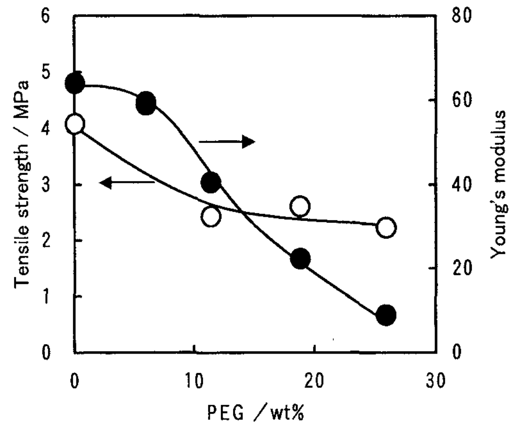

Fig. 5 The tensile strength and Young's modulus of the SPEs using the $POEM_5$ graft copolymer as a function of PEG content (POEM content=48wt%).

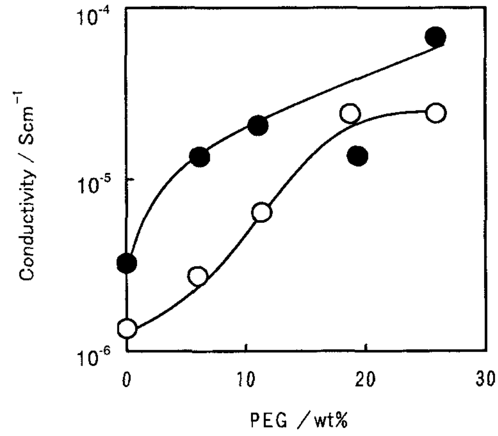

Fig. 6 The ionic conductivity of the SPEs as a function of PEG content. (●): SPE made from $POEM_5$ (POEM content=48wt%), (○): SPE made from $POEM_9$ (POEM content=35wt%)

3.4 Ionic conductivity of the SPEs

Figure 6 shows the ionic conductivity of SPEs at 23°C as a function of PEG content. The ionic conductivity of the two SPEs increases with increasing PEG content. The ionic conductivity of the SPE made from $POEM_5$ has higher values than that from $POEM_9$ because of the high POEM content. The value of the ionic conductivity of the SPE made from $POEM_5$ is 6×10^{-5} S/cm at 23°C.

4. CONCLUSIONS

We synthesized a hyper-branched graft polymer synthesized by graft polymerization of poly(MMA-co-CMS) macroinitiator on POEM macromonomer using ATRP. The ^1H NMR spectroscopic analysis of the hyper branched graft copolymer confirms the proposed structure of the graft copolymer. Solid polymer electrolytes were prepared from the polymer obtained, $LiClO_4$ and polyethylene glycol dimethylether (PEG), changing PEG content. Although both the tensile strength and Young's modulus decrease with increasing PEG content, the tensile strength has 3MPa even when PEG content is 28wt%. The ionic conductivity of the SPEs increasing with PEG content is 6×10^{-5} S/cm at room temperatures and the tensile strength was over 2MPa. These results indicate that a SPE prepared from the hyper-branched graft copolymer has potential to be applied to a solid polymer electrolyte.

5. ACKNOWLEDGMENT

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6. REFFERENCES

[1]J.R. MacCallum, C.A. Vincent, *Polymer Electrolyte Reviews 1 and 2, Elsevier: London* (1987, 1989).

[2]F.M. Gray, *Solid Polymer Electrolytes, VCH Publishers: New York*, 1991.

[3] B. Scrosati, *Applications of Electroactive Polymers, Chapman and Hall, London*, 1993.

[4]P.P. Soo, B. Huang, Y.-I. Jang, Y.-M. Chiang, D.R. Sadoway, and A.M. Mayes, *J. Electrochem. Soc.*, 146, 32 (1999).

[5]M. Watanabe, S.-I. Oohashi, K. Sanui, N. Ogata, T. Kobayashi and Z. Ohtaki, *Macromokecules*, 18, 1945 (1985).

[6]J.R.M. Giles, F.M. Gray, J.R. MacCallum and C.A. Vincent, *Polymer*, 28, 1977 (1987).

[7]F.M. Gray, J.R. MacCallum, C.A. Vincent and J. R.M. Giles, *Macromolecules*, 21, 392 (1988).

[8]I. Khan, D. Fish, Y. Delaviz and J. Smid, *Makromol. Chem.*, 190, 1069 (1989).

[9]J. Li and I. Khan, *Makromol. Chem.*, 192, 3043 (1991).

[10]S. Kohjiya and Y. Ikeda, *Mater. Sci. Res. Int.*, 4, 73 (1998).

[11]H.R. Allcock, R.Prange and T.J. Hartle, *Macromolecules*, 34, 5463 (2001).

[12]D.R. Sadoway, A.M. Mayes, B. Huang, S.Mui, P.P. Soo, D.H. Saelin and C. Cook, *J. Power Sources*, 97-98, 621 (2001).

[13]A.-V.G. Ruzette, P.P. Soo, D.R. Sadoway and A.M. Mayes, *J. Electrochem. Soc.*, 148, A537 (2001).

[14]J. Saunier, F. Alloin and J.-Y. Sanchez, *Electrochim. Acta*, 45, 1255 (2000).

[15]P.E. Trapa, B. Huang, Y-Y. Won, D.R. Sadoway and A.M. Mayes, Electrochem. *Solid-state Let.*, 5 A85 (2002).

[16]J.F. Hester, P. Banerjee, Y.-Y. Won, A. Akthakul, M.H. Acar and A.M. Mayes, *Macromolecules*, 35, 7652 (2002).

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