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Block-type proton exchange membranes prepared by a combination of radiation-induced grafting and atom-transfer radical polymerization

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Abstract

We prepared proton exchange membranes (PEMs) composed of block-type polymers by a combination of radiation-induced graft polymerization (RIGP) and atom-transfer radical polymerization (ATRP). This process involves the following three steps: (i) RIGP of styrene (St) and chloromethylstyrene (CMS) into poly(ethylene-*co*-tetrafluoroethylene) (ETFE) films; (ii) the ATRP of ethyl styrene sulfonate (EtSS) starting from the grafted CMS units; and (iii) hydrolysis of the EtSS-grafted film, converting poly(EtSS) to poly(styrene sulfonic acid) (PSSA). The ATRP of EtSS (step (ii)), the key process in our preparation method, was successfully performed by controlling the catalyst concentration at a relatively-low temperature (50 ºC), under the condition of which undesirable thermal polymerization was suppressed. The grafting degree during ATRP could be controlled and ranged from 24% to 240%, resulting in the preparation of PEMs with ion exchange capacities ranging from 0.96 to 2.9 mmol/g. Thus, we have demonstrated that ATRP reactions can be carried out inside solid polymer films. At 30% relative humidity and 80 ºC, the block-type PEMs exhibited higher proton conductivities and water contents than those of the conventional RIGP-PEMs. In the block-type PEMs, the hydrophilic proton-conducting PSSA grafts are separated from the ETFE matrix by the hydrophobic polystyrene grafts. Hence, the PSSA-graft-chain aggregation occurs, creating a well-connected ion channel network, which in turn results in increased proton conduction.