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High Tg sulfonated insertion polynorbornene ionomers prepared by catalytic insertion polymerization

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ABSTRACT

A simple method to synthesize high Tg sulfonated ionomers based on catalytic insertion polynorbornene is reported. Copolymers of norbornene and 5-methyl alcohol norbornene (*endo*:*exo* = 82:18) or 5-methyl bromide norbornene (*endo*:*exo* = 86:14) as well as terpolymers of norbornene, 5-methyl alcohol norbornene and 5-hexyl norbornene are prepared using a cationic Pd catalyst. These copolymers are then thioacetylated. Using hydrogen peroxide as oxidant, a sulfonated polynorbornene is obtained. Ionomers containing as much as 30 mol% SO_3H and with Tgs above 200 °C are obtained in a four-step procedure of overall 40–75% yield.

1. Introduction

Currently, Nafion is the state-of-the-art commercial proton exchange membrane (PEM) used in fuel cell devices [1]. Its high ionic conductivity, good chemical and mechanical stability even when swollen by water makes it an excellent candidate for such an usage. Protons can diffuse through hydrated channels which originate from a microphase separation between the hydrophobic polytetrafluoroethylene backbone and polar domains containing the sulfonic acid moieties [2]. However, at temperatures higher than 100 °C, Nafion loses its mechanical strength when well hydrated [3]. In order to address this issue, several high Tg sulfonated polymers such as polyetherketones, polyimides, polybenzimidazoles, polyarylether and polyphosphazenes have been scrutinized [1,4–7]. Polymers based on vinyl monomers have also been studied such as grafted sodium poly(styrene sulfonate) chains on polyethylene [8,9], on poly(ethylene-co-tetrafluoroethylene) [10] or polyvinylidene fluoride [11]. Nonetheless, currently no polymer completely fulfills the stringent set of conditions (conductivity, stability, durability, cost, etc …) required for functional sulfonated PEMs operating at temperatures above 100 °C. Thus, the search for novel high Tg sulfonated ionomers is the object of intense research [1,4].

Recently, it has been demonstrated that insertion polynorbornenes (PNBE) could successfully be used for the preparation of PEMs [12–16]. This polymer is particularly promising as it exhibits a glass-transition temperature (Tg) around 350–400 °C and an excellent chemical stability stemming from its saturated backbone [17]. Such PNBE is obtained by the insertion polymerization of norbornene (NBE) and its properties are vastly different from the PNBE obtained by ring-opening metathesis polymerization. Wang et al. [14] cross-linked insertion PNBE with 4,5-imidazole dicarboxylic acid (IDA) and doped it with phosphoric acid. The resulting membranes were stable up to 280 °C and their conductivities reached 3.05 mS cm^{-1} at 80 °C. He et al. [13], prepared an anion exchange membrane based on PNBE, with conductivity as high as 4.14 mS cm^{-1} at 80 °C. Daigle et al. [12] prepared proton exchange membranes based on a terpolymer of ethylene, norbornene and norbornene-5-*exo*-methyl sulfonic acid, using *exo* monomers only (as *endo* monomers are usually not reactive [18]). The resulting PEM exhibits a moderate conductivity at 100 °C. Although it appears that the PNBE backbone can be exploited for the design of ionomers as fuel cell membranes, the preparation of these ionomers remains challenging and time-consuming. Recently, we demonstrated that the sulfonic moiety could readily be introduced by oxidation of the thioacetate moiety with H_2O_2, thus precluding the need of corrosive chlorosulfonic acid as sulfonation agent [12]. However, the preparation of insertion PNBE bearing pendant thioacetate groups,

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and more generally the preparation of any PNBE bearing pendant polar groups, is complicated by the fact that only a low number of catalysts are able to insert polar norbornenes [19,20]. Furthermore, substituted NBEs containing heteroatoms in *endo* conformation can actually significantly retard or even stop the polymerization [18,19]. Under standard laboratory conditions, the Diels–Alder reaction usually forms a polar norbornene monomer containing more than 50% *endo* isomer. The *endo* isomer must be separated from the *exo* one prior polymerization if a high polymerization yield is targeted. Recently, we have demonstrated that the lack of reactivity of the *endo* monomer can be bypassed via the rectification-insertion mechanism, whereby the catalyst not only promotes the monomer insertion, but also catalyzes the isomerization of the *endo* monomer into *exo* monomer. We here demonstrate that the rectification-insertion mechanism can be used for the polymerization of norbornene-5-methyl bromide (NBE-CH_2Br) and norbornene-5-methyl alcohol (NBE-CH_2OH) and its copolymerization with norbornene and alkyl norbornenes. Remarkably, as none of the *endo* and *exo* isomers are separated, this synthetic scheme (Scheme 1) represents a very simple route toward the synthesis of PNBE-based sulfonated ionomers. In this study, our goal is to prepare ionomers based on insertion PNBE, in order to benefit from the very high Tg and chemical robustness of this polymer. In order to introduce proton conducting moieties, a substituted norbornene (NBE-CH_2OH or NBE-CH_2Br) is copolymerized and then converted to sulfonic group (Scheme 1). Furthermore, to improve the processability of the resulting copolymer, a third monomer, 5-hexylnorbornene (NBE-Hxl) is also copolymerized. Thus terpolymers of NBE, NBE-Hxl and a norbornene unit containing a pendant SO_3H were prepared and were shown to be interesting candidates for preparing PEM.

2. Experimental

2.1. Materials and general considerations

All the manipulations that involved air and/or moisture sensitive compounds were performed using a nitrogen filled glove-box. All chemicals were purchased from Sigma–Aldrich and were stored under nitrogen. Allyl alcohol, allyl bromide and 1-octene were distilled prior utilisation in Diels–Alder reactions. Liquid monomers used for polymerization reactions were dried over molecular sieves and deoxygenated by bubbling the liquids with nitrogen prior insertion into the glove-box. Solvents used for the mesylation and thioacetylation reactions such as THF, DMF and Toluene were obtained from a solvent purification system from mBraun.

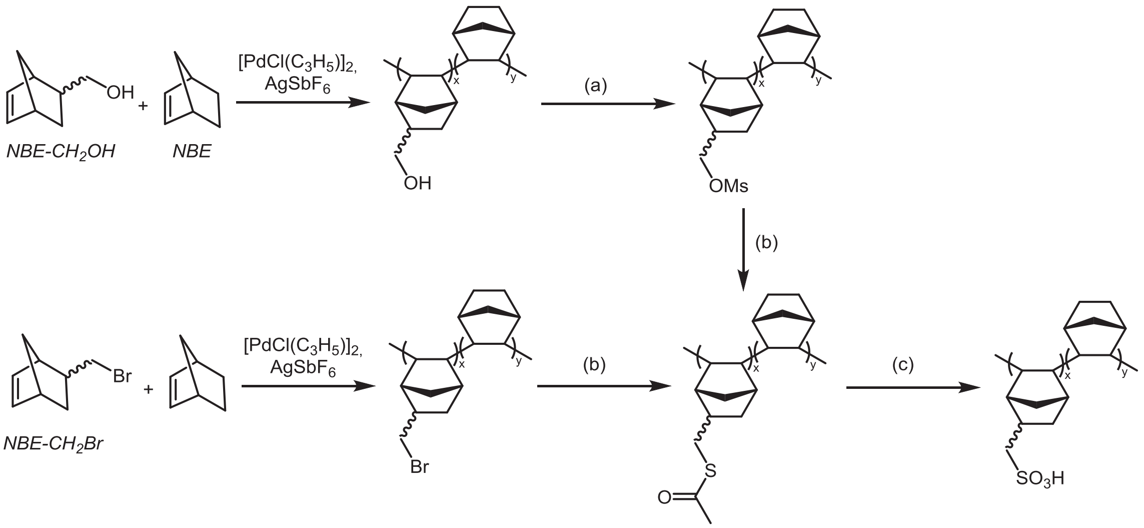
2.2. Instrumentation

^1H, ^{13}C NMR spectra were recorded on a Bruker Ultrashield 300 MHz at ambient temperature and ^1H chemical shifts were referenced to the solvent signal. The solid polymers FTIR spectra were recorded on a Nicolet 6700 Spectrometer equipped with Smart ATR accessory. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) using a Viscotek HT GPC instrument equipped with three columns, 2 PLGel 10 μm Mixed B LS and 1 Agilent PLGel 20 μm Mixed ALS and running in THF at 40 °C. Glass transition temperatures (T_g) were measured by differential scanning calorimetry (DSC) using a DSC1 Mettler Toledo device using a 10 °C/min heating and cooling scan. The second heating ramp was used to determine Tg.

2.3. Synthesis of norbornene-5-methyl alcohol NBE-CH_2OH

The synthesis of the different monomers used was performed in a Parr pressurized reactor (300 mL) as pressures ranging from 100 to 200 psi were attained depending on the reaction temperature. Dicyclopentadiene (DCPD) (100 g, 0.76 mol, 1.0 eq) and allyl alcohol (62 g, 1.06 mol, and 1.4 eq) were added to the reaction vessel and the mixture was heated at 210 °C for 2 h while stirred at a speed of 600 rpm. The resulting mixture was cooled down and was then poured into a 250 mL round-bottom flask fitted with a simple distillation apparatus under vacuum. The resulting NBE-CH_2OH was distilled twice, yielding a viscous and colorless oil (yield 56%) (*Endo/exo*: 82/18).

Endo: ^1H NMR (300 MHz, $CDCl_3$, δ): 6.06 (dd, $J = 5.6$, 3.0 Hz, 1H), 5.89 (dd, $J = 5.6$, 2.9 Hz, 1H), 3.28 (dt, $J = 17.4$, 8.7 Hz, 1H), 3.13 (t, $J = 8.6$ Hz, 1H), 2.86 (d, $J = 22.1$ Hz, 1H), 2.72 (s, 1H), 2.22 (s, 1H), 1.74 (ddd, $J = 11.8$, 9.2, 3.8 Hz, 1H), 1.13–1.38 (m, 3H), 0.46 (ddd, $J = 11.8$, 4.3, 2.7 Hz, 1H) (See Fig. S1); ^{13}C NMR (60 MHz, $CDCl_3$, δ) 132.2, 137.2, 66.0, 49.4, 43.5, 42.2, 41.5 and 28.8 (See Fig. S2).



Scheme 1. Preparation of the sulfonated PNBE (a) Toluene, THF (both anhydrous), Mesyl Chloride, Et_3N, reflux, 6 h. (b) Toluene, DMF (both anhydrous), Potassium thioacetate, reflux 12 h (c) H_2O_2 30% w/w in H_2O, AcOH, iPrOH, 65 °C, 12 h.