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One-pot synthesis of high molecular weight sulfonated poly(oxadiazole–triazole) copolymers for proton conductive membranes

Mariela L. Ponce*, Dominique Gomes, Suzana P. Nunes

GKSS Research Centre Geesthacht GmbH, Institute of Polymer Research, Max Planck Str. 1, D-21502 Geesthacht, Germany

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ABSTRACT

For the first time, a series of high molecular weight ($1–4 \times 10^5\,\mathrm{g\,mol^{-1}}$) sulfonated poly(oxadiazole–triazole) copolymers have been synthesized at high temperatures and very short reaction time, by a single-step method based on solution polycondensation reaction of non-sulfonated dicarboxylic acid, hydrazine sulphate and aromatic primary amine (sulfonated and non-sulfonated) in poly(phosphoric acid). By this fast synthetic procedure, copolymers with a high conversion to triazole groups (up to 93%) as well high sulfonation level (IEC = 1.17–1.84 mequiv. $\mathrm{g^{-1}}$) have been obtained. The structure of the polymers was characterized by elemental analysis and ^{1}H NMR.

Since high sulfonation levels (IEC = 1.17–1.84 mequiv. $\mathrm{g^{-1}}$) could be obtained, membranes were prepared from these polymers and have been characterized aiming the application in fuel cells. Proton conductivity up to $6 \times 10^{-2}\,\mathrm{S\,cm^{-1}}$ at 150 °C was measured. The polymer films had good mechanical properties with storage modulus of about 3 GPa at 300 °C. These films exhibited high thermal stability with T_g up to around 440 °C.

1. Introduction

The conventional proton conductive membranes like Nafion® are manufactured from sulfonated polymers. Proton conductivity in these cases requires high hydration levels and the proton transport is in great extent promoted by water movement inside the membrane. Sulfonated membranes tend to lose conductivity above 100 °C due to dehydration, hence the maximum operation temperature of a polymer electrolyte fuel cell is usually kept below the boiling point of water, although at higher temperatures would bring considerable advantages from the point of view of reaction kinetics and catalyst susceptibility to contaminants. To overcome this drawback several groups are searching worldwide for alternative membranes able to transport protons by other mechanisms or at least able to properly operate at a broader temperature range and at lower humidification levels. The most investigated material for this condition is polybenzimidazole (PBI), which was introduced by Savinell and Litt [1] and is today after manufacture in membrane-electrode assembly commercialized by BASF Fuel Cell. Pristine PBI has negligible proton conductivity, but when doped with phosphoric acid (ca. five H_3PO_4 molecules per PBI unit) the proton conductivity reaches values of 60 mS/cm at 180 °C, as mentioned in an extensive review on PBI membranes recently published by Li and Jensen [2,3]. The idea behind it is that PBI contain rather basic groups, which act as proton acceptor in an acid–base “reaction” with the doping acid. In ideal case after protonation the imidazole group should be able also to donate the proton back to an acid molecule and further promote its effective migration. However this is not the only and not even the main event involved in the proton transport in PBI. Actually a large amount of free acid molecules is present and in great part they act as vehicle for the proton transport. The well-known disadvantage is that under operation this acid can be leached out of the membrane. Another disadvantage of PBI is the low proton conductivity at room temperature even when acid-doped. When aiming application in the automotive industry this is also an important issue. In the last years a lot of efforts have been dedicated to improve PBI membranes by changing their chemical structure, like is reported in a review of Leikin et al. [4]. A strategy has been the introduction of sulfonic groups [5]. Promising results have been reported by incorporating pyridine into the backbone [6,7]. Our group has been investigating another class of polymers, also containing amphoteric heterocyclic groups, which could act as proton acceptor and donor. A series of papers based on polyoxadiazole has been published [8–11]. Here in this paper the focus is on polytriazoles. As mentioned before for working well not only basicity is required but the polymer must be able also to donate protons and therefore a very well balanced amphoteric character must be offered, otherwise the proton transfer might be blocked. Triazole and oxadiazole groups are less basic than pyridine and are expected to offer more convenient amphoteric sites for proton transfer. Fur-

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* Corresponding author. Tel.: +49 4152 87 2472; fax: +49 4152 87 2466.
E-mail address: mariela.ponce@gkss.de (M.L. Ponce).

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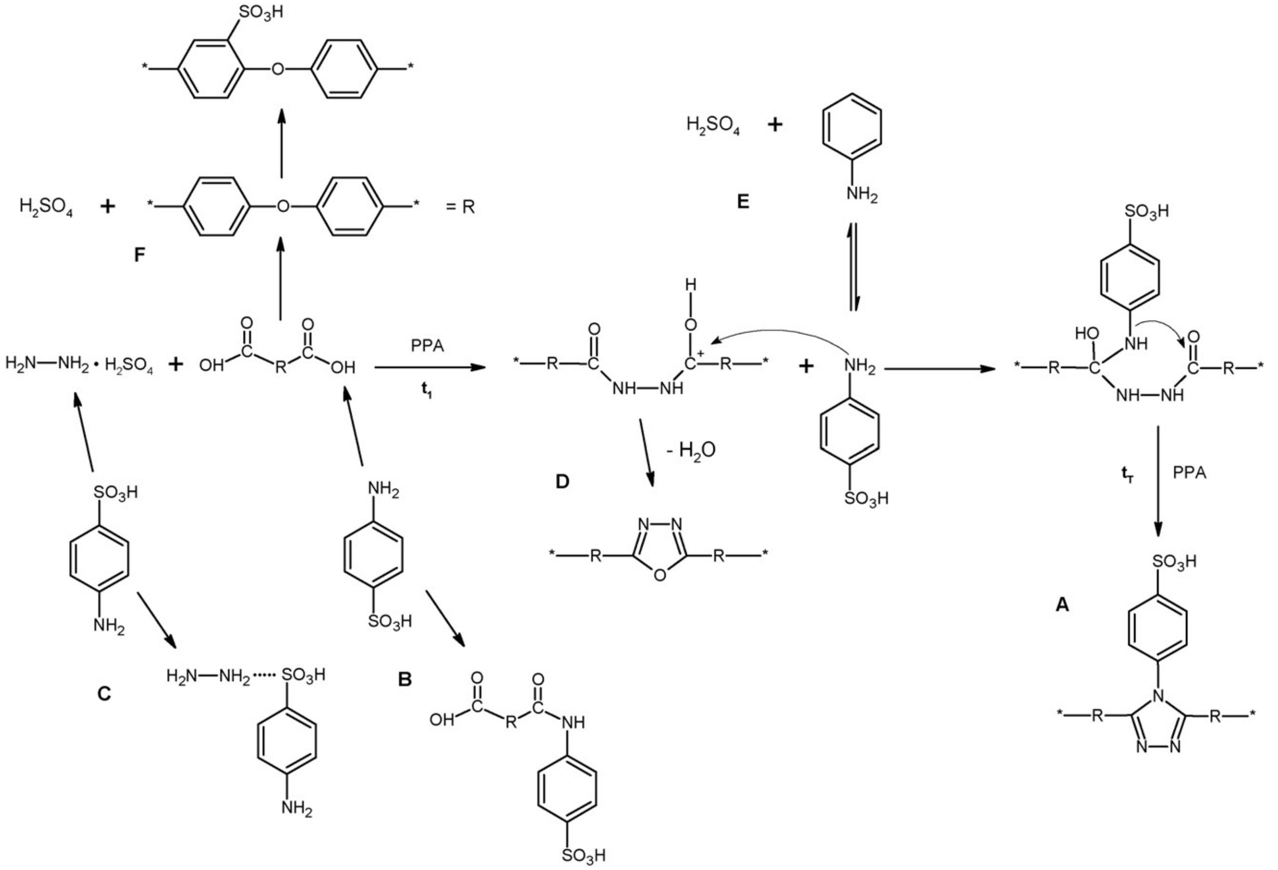

Fig. 1. Proposed main and side reaction mechanisms for the one-pot synthesis of polytriazole polymers.

thermore acid sulfonic group could be additionally introduced. Both the amphoteric triazole/oxadiazole groups and the acid sulfonic groups are favorable sites for hydrogen bonding.

So far the reason for choosing polytriazole is explained above but this is only the first step. The most important issue in this paper is how to synthesize polytriazole with a rather simple and fast method and leading to a product not only with high proton conductivity but also with good enough mechanical properties to prepare membranes and in a future stage to manufacture them into stable membrane-electrode assemblies.

The literature describes different routes for the synthesis of polymers containing the 4-phenyl- or 4-hydro-1,2,4-triazole unit in the structural backbone or as pendant groups [12]. The reaction between ditetrazoles and diacid chlorides affords relatively low molecular weight polymers. On the other hand high molecular weight polymers can be obtained by the cyclocondensation reaction of aniline with aromatic polyhydrazides in polyphosphoric acid (PPA). However the conversion from polyhydrazides to polytriazoles is not always high. If polytriazoles are expected to be produced in a large scale, there is a need to synthesize high molecular weight polytriazoles in short reaction time at high temperatures without residual hydrazide groups and soluble in common polar aprotic organic solvents.

In this paper, we describe a short time one-pot synthesis of high molecular weight sulfonated poly(1,3,4-oxadiazole–1,24-triazole)s and the effect of the synthesis conditions (initial reaction time, t_1, and total reaction time, t_T) on the polymer properties, specially taking into account the conversion degree and sulfonation level, for their application in fuel cells. The one-stage synthesis of polytriazoles is not only of technologically but also of economically convenience compared to multiple-stage process. Therefore, sulfonated poly(oxadiazole–triazole)s copolymers were synthesized via one-step polycondensation reaction of hydrazine sulfate, a non-sulfonated dicarboxylic acid and aromatic primary amine (sulfonated and non-sulfonated) in polyphosphoric acid. The reaction time (t_1 and t_T) effect on the degree of conversion (N/C ratio) to polytriazoles was investigated. By using an aromatic primary amine containing in its structure at least one sulfonic acid group the sulfonation level (S/C ratio) was controlled. According to Fig. 1, an optimum t_1 will allow the polymerization to take place following mechanism A, i.e., the synthesis of poly(4-phenyl-1,2,4-triazoles) with higher N/C and S/C values by cyclocondensation reaction between an intermediate polyhydrazide and an aromatic primary amine (e.g. aniline or sulfonated aniline).

2. Experimental

2.1. Materials

All chemicals were used as received. Aniline, ANI (≥99%, Aldrich); 4-aminobenzenesulfonic acid, S-ANI (99%, Aldrich); 4,4′-diphenylether dicarboxylic diacid, DPE (99%, Aldrich); hydrazine sulphate, HS (>99%, Aldrich); poly(phosphoric acid), PPA (115% as H_3PO_4, Aldrich); sodium hydroxide, NaOH (99%, Vetec); hydrochloric acid (fuming 37%, Aldrich); *N*-methyl-2-pyrrolidone, NMP (Merck); dimethyl sulfoxide, DMSO (Merck), dimethylacetamide, DMAc (Merck); dimethylformamide, DMF (Merck).

2.2. Synthesis of sulfonated poly(oxadiazole–triazole) copolymers

The general synthesis procedure can be described as follow: PPA was initially heated up to 100 °C in a 500-ml three-necked flask