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CHEMISTRY

New Poly(1,2,3-triazolesulfonic acids) for Proton Exchange Membranes of Fuel Cell

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Fuel cells (FCs) based on proton exchange membranes are promising as electric power sources. They provide a possibility to receive energy from hydrogen, synthetic or biosynthetic fuel and can operate with higher efficiency as compared with heat engines [1, 2].

Hydrated sulfonic-acid polymer-electrolyte proton exchange membrane (PEM) in an FC provides a transfer of protons resulting from electrochemical oxidation of fuel on anode to cathode and separates anode and cathode space.

Polymer films used as PEMs in FCs, in particular, in low-temperature fuel cells operating at 60–90°C, should meet a number of stringent and conflicting requirements, which are not always fulfilled. Thus, the most widespread perfluorinated PEM Nafion®, which shows excellent mechanical properties and proton conduction in a hydrated state, readily loses water above 60°C and can provide fuel cell performance only under conditions of forced humidification (≥80% humidity), which decreases the total efficiency of cell and makes its design more complicated [1–4].

Films alternative to Nafion®, so-called hydrocarbon membranes based on sulfonated aromatic heterochain polymers and a number of polyheteroarylenes, which show comparable performance characteristics and rather low cost, have much lower durability than Nafion® [2–4]. Therefore, the search for methods for the synthesis of new types of proton exchange film-forming polymers is an important task of polymer chemistry.

EXPERIMENTAL

Dimethyl sulfoxide (DMSO), sodium nitrite, sodium azide, potassium carbonate, propargyl bromide, propargyl alcohol, 4,4'-diaminostilbene-2,2'-disulfonic acid, hydroquinone, 4,4'-isopropylidenediphenol, cyanuric chloride, metanilic acid, sodium hydroxide from Acrus were used without additional purification.

1,3,5-Triethinylbenzene (**6**) from Alfa Aesar and 2,2'-benzidinedisulfonic acid from Kodak were also used without additional purification.

^{1}H NMR spectra of studied compounds were recorded on a Bruker Avance^{TM} 400 spectrometer operating at 400.13 MHz in DMSO-d_6 solution. Chemical shifts δ were determined using residual proton signals of the deuterated solvent as an internal reference.

Thermogravimetric (TGA) studies of polymers were carried out on an MOM Q-1000 derivatograph (Hungary) in air at a heating rate of 5 K/min with a sample weight of ~20 mg.

Thermomechanical (TMA) studies were performed in air at a heating rate of 2.5 K/min, load of 100 g, rod diameter of 4 mm, $\sigma = 0.08$ MPa.

The IR absorption spectra of samples were recorded as thin films or as KBr pellets on a Nicolet Magna-IR 750 FTIR spectrophotometer in the range 4000–400 cm^{-1}.

Reaction course and purity of isolated products were monitored by TLC on Silufol UV-254 plates. Visualization under UV light.

Reduced viscosity was measured with a capillary Ubbelohde viscometer at a polymer concentration of 0.5 g/dL in *N*-methylpyrrolidone at 25°C.

Synthesis of Monomers and Sodium 3-Azidobenzenesulfonate

Aromatic diazides **1** and **2** with sulfonic groups (Scheme 1) are not described in the literature but readily obtained from corresponding diamines by standard procedures: diamines were first subjected to diazotization according to [6], then the resultant dia-

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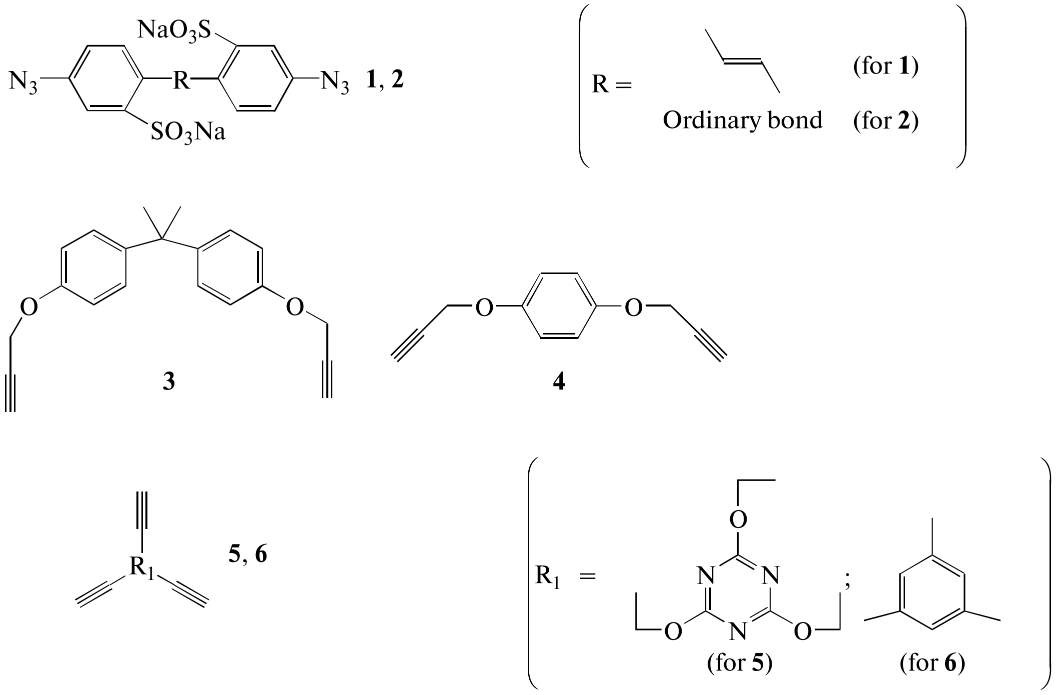
Monomer structure



Scheme 1.

zonium salts were reacted on cooling with a 10% molar excess of a 20% aqueous sodium azide solution. The azides were isolated after partial removal of water on a rotary evaporator and then were recrystallized from water or ethanol. The yield of the products after recrystallization was 70–75%.

Compound 1. ^{1}H NMR (δ, ppm): 7.14 (dd, 2H, HC-5,5', $^4J_{HH} = 3.2$ Hz, $^3J_{HH} = 11.1$ Hz), 7.52 (d, 2H, HC-3,3', $^4J_{HH} = 3.2$ Hz), 7.65 (d, 2H, HC-6,6', $^3J_{HH} = 11.1$ Hz), 8.05 (s, 2H, HC_{vinyl}). IR (ν, cm^{-1}): 2117 (N_3), 1189, 1080, 1023 (SO_3^-).

Compound 2. ^{1}H NMR (δ, ppm): 6.93–7.00 (m, 2H, HC-5,5'), 7.31–7.38 (m, 2H, HC-6,6'), 7.65 (s, 2H, HC-3,3'). IR (ν, cm^{-1}): 2116 (N_3), 1233, 1205, 1043, 1032 (SO_3^-).

Sodium 3-azidobenzenesulfonate (**7**) was obtained similarly to compound **2** as described in [7]. ^{1}H NMR (δ, ppm): 7.04–7.09 (m, 1H, HC-4), 7.27–7.31 (m, 1H, HC-2), 7.38 (t, 1H, HC-5, $^3J_{HH} = 7.6$ Hz), 7.42 (d, 1H, HC-6, $^3J_{HH} = 7.6$ Hz). IR (ν, cm^{-1}): 2107 (N_3), 1213, 1175, 1047 (SO_3^-).

Dipropargylic ethers of 4,4'-isopropylidenediphenol (**3**) and hydroquinone (**4**) (Scheme 1) were obtained by reacting the initial diphenols with propargyl bromide in the presence of K_2CO_3 according to the known procedures [8].

Compound 3: mp. 77–79°C (lit. 74–76°C), yield 85%.

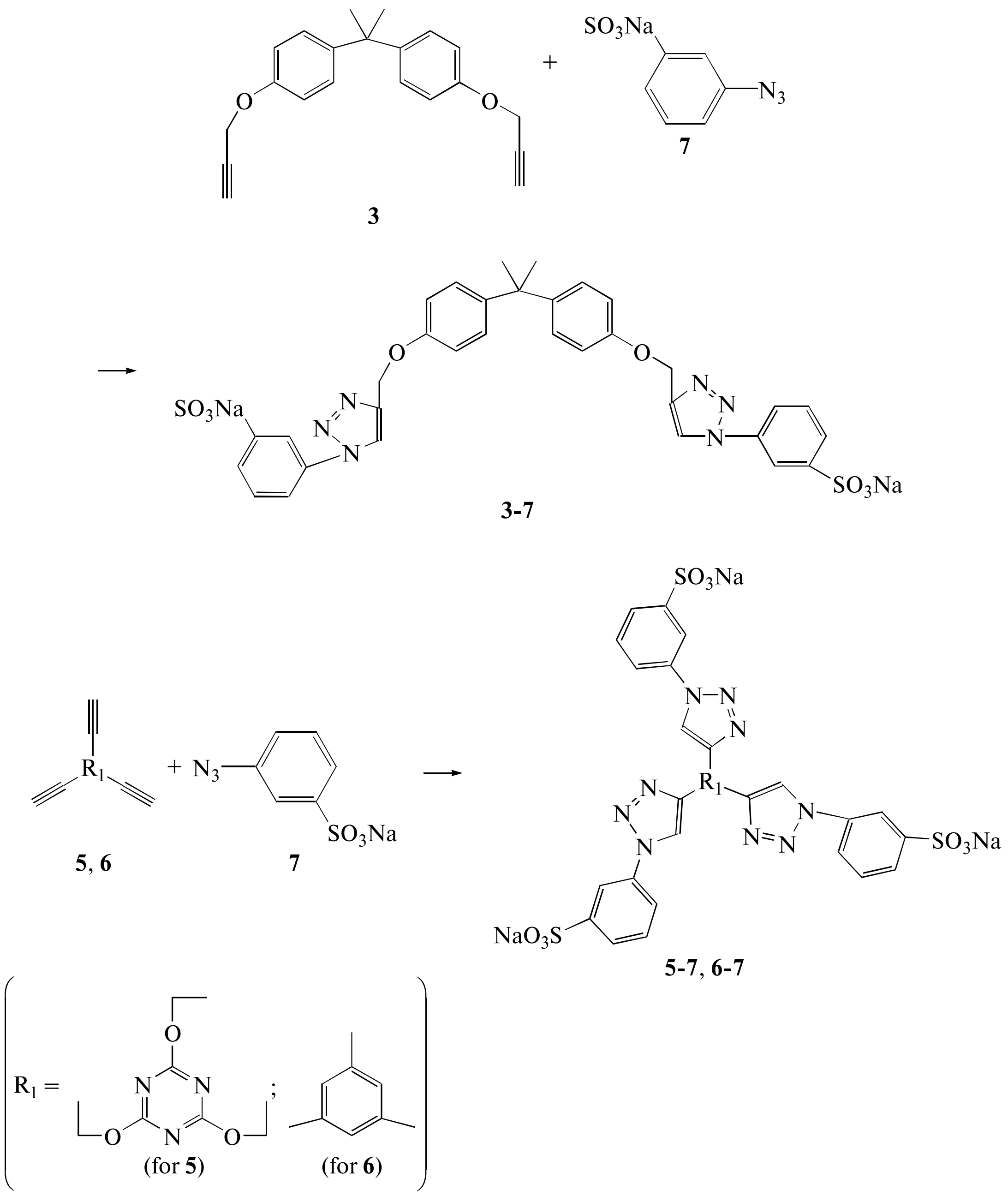
Compound 4: mp. 41–43°C (lit. 49–51°C), yield 75%.

2,4,6-Tris(2-propynyloxy)-1,3,5-triazine (**5**) (Scheme 1) was obtained from cyanuric chloride and propargyl alcohol in the presence of sodium hydroxide by the known procedure [9]. Mp 73–75°C (lit. 77–78°C), yield 79%.

Synthesis of model compounds 3-7, 5-7, and 6-7

The reactions of compounds **3**, **5**, and **6** with compound **7** (Scheme 2) were carried out in DMSO at 70–100°C and total concentration of initial compounds of 0.5 g/mL during 6 h, CuI was used as a catalyst in amount of 10 mol %. The yield of products **3**-**7**, **5**-**7**, and **6**-**7** after purification was at least 85%; the compounds were characterized by ^{1}H NMR and FTIR spectroscopy. IR spectra show the lack of absorption at 2100–2120 cm^{-1} typical for azide group, as well as at

Synthesis of model compounds



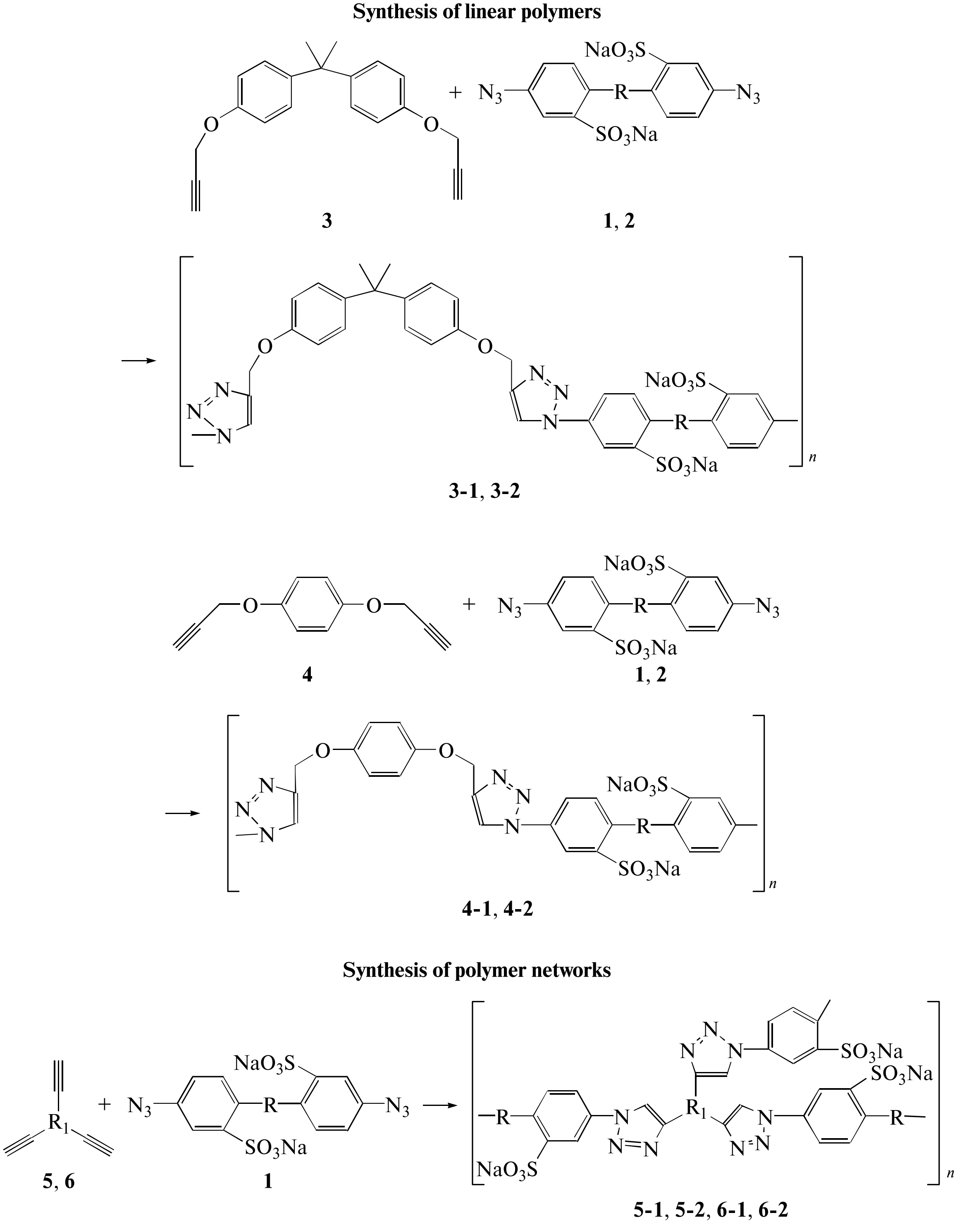
Scheme 2.

3260–3290 and 2110–2140 cm^{-1} inherent in terminal acetylene group.

Compound 3-7. ^1H NMR (δ, ppm): 9.00 (s, 2H, $HC_{triazole}$), 8.12 (s, 2H, $HC_{arom.}$), 7.87 (d, 2H, $HC_{arom.}$, $^3J_{HH}$ = 7.1 Hz), 7.72 (d, 2H, $HC_{arom.}$, $^3J_{HH}$ = 7.1 Hz), 7.58 (t, 2H, $HC_{arom.}$, $^3J_{HH}$ = 7.4 Hz), 7.15 (d, 4H, $HC_{arom.}$, $^3J_{HH}$ = 8.1 Hz), 6.99 (d, 4H, $HC_{arom.}$, $^3J_{HH}$ = 8.1 Hz), 5.19 (s, 4H, CH_2), 1.61 (s, 6H, CH_3).

Compound 5-7. ^1H NMR (δ, ppm): 9.04 (s, 3H, $HC_{triazole}$), 8.13 (s, $HC_{arom.}$), 7.87 (d, 3H, $HC_{arom.}$, $^3J_{HH}$ = 7.8 Hz), 7.72 (d, 3H, $HC_{arom.}$, $^3J_{HH}$ = 7.6 Hz), 7.58 (t, 3H, $HC_{arom.}$, $^3J_{HH}$ = 7.8 Hz), 5.64 (s, 6H, CH_2).

Compound 6-7. ^1H NMR (δ, ppm): 9.61 (s, 3H, $HC_{triazole}$), 8.66 (s, 3H, $HC_{arom.}$), 8.27 (s, 3H, $HC_{arom.}$), 8.04 (d, 3H, $HC_{arom.}$, $^3J_{HH}$ = 7.6 Hz), 7.77 (d, 3H, $HC_{arom.}$, $^3J_{HH}$ = 7.5 Hz), 7.65 (t, 3H, $HC_{arom.}$, $^3J_{HH}$ = 7.8 Hz).



Scheme 3.

Synthesis of Linear Polymers

Synthesis of polymers **3-1**, **3-2**, **4-1**, **4-2** (Scheme 3) was carried out in DMSO under conditions similar to the model reactions. Polymerization of equimolar amounts of diazides and dipropargyl ethers proceeds smoothly at concentrations of 0.4–0.5 g/mL at 60–100°C during 10–12 h in the presence of 5–10 mol % of CuI. The polymers were precipitated with isopropanol or films were obtained immediately by pouring reaction mixture on a glass followed by evaporation of the solvent. The polymers were characterized by viscometry, ^{1}H NMR and IR spectroscopy, TGA, and TMA data (Table 1). The ^{1}H NMR spectrum of polymer **3-2** with $\eta_{red} = 0.6$ dL/g is exemplified below.

Compound 3-2. ^{1}H NMR (δ, ppm): 9.00 (s, 2H, $HC_{triazole}$), 8.40 (s, 2H, $HC_{arom.}$), 7.78 (m, 2H, $HC_{arom.}$), 7.58 (m, 2H, $HC_{arom.}$), 7.17 (m, 4H, $HC_{arom.}$), 7.00 (m, 4H, $HC_{arom.}$), 5.22 (s, 4H, CH_2), 1.61 (m, 6H, CH_3).

A film obtained from polymer **4-1** was also characterized by strength test (Table 2).

Synthesis of Polymer Networks

Polytriazole networks **5-1**, **5-2**, **6-1**, and **6-2** (Scheme 3) were obtained by pouring a preliminary filtered 3–4% solution of monomers and CuI (5–10 mol % of the sum of moles of the monomers) in DMSO on a glass support (Petri dish) followed by evaporation of the solvent on heating to 40°C for 10–20 h. The degree of reaction was determined from the decrease in the intensity of the absorption band of azide group at 2100–2120 cm^{-1} in the IR spectra of resultant films.

The films prepared from polytriazoles **5-1** and **6-1** (Table 2) were characterized by strength tests.

Table 1. Physicochemical characteristics of linear PTA

Polymer (in Na form)	η_{red}, dL/g	T_d, °C	$T_{5\%}$, °C	IC, mol equiv/g*
3-1	0.8	330	160	2.76
3-2	0.6	260	160	2.86
4-1	0.6	220	160	3.33
4-2	0.4	290	160	3.43

* Calculated ion-exchange capacity.

Table 2. Physicomechanical characteristics of selected PTAs

Polymer (in Na form)	σ, MPa	ε, %	$E \times 10^{-3}$, MPa
5-1	70.1	5.1	2.3
6-1	127.0	5.5	3.7
6-1 (H form)	121.8	7.8	3.4
4-1	56	4.5	1.8

RESULTS AND DISCUSSION

One of the possible ways to solve the above-noted problems is the transfer from traditional reactions to organic reactions unconventional for polymer chemistry, in particular, to click reactions, among which the Huisgen reaction, a 1,3-dipolar azide cycloaddition to terminal acetylenes in the presence of monovalent copper salts to form 1,2,3-triazoles in high yields, is an important one. Poly(1,2,3-triazoles) (PTAs) can be more stable toward oxidation and hydrolysis than heterochain polymers because it was reported in the literature that the triazole ring shows high stability toward attacks of oxidizing agents and water and elevated temperature [5].

Until now, the Huisgen reaction has been little used for the synthesis of linear polymers because authors failed to prepare high-molecular-weight products suitable for manufacturing strong films and fibers [10, 11], while there was no attempt to obtain proton exchange polytriazoles.

In the context of work on the design of new polymeric materials for proton exchange membranes (PEM) of low-temperature fuel cells, we prepared for the first time high-molecular-weight film-forming polytriazoles **3-1**, **3-2**, **4-1**, **4-2**, **5-1**, **5-2**, **6-1**, and **6-2** containing sulfonic groups on the basis of sulfonated aromatic diazides **1** and **2** as well as two- and three-functional terminal alkynes **3**–**6** (Scheme 3). It should be noted that the main driving force of this study is the obvious simplicity of preparation of the monomers and polymers and evident availability of starting materials for their synthesis.

To prove the possibility of polymer synthesis, we first studied in detail the features of the Huisgen reaction with azides containing sulfonic groups using model compounds (Scheme 2). We prepared a series of triazoles modeling the monomer unit of linear or polytriazole networks.

The synthesis of linear polymers was carried out using the equimolar ratio of diazide and diacetylene in DMSO medium at 60–100°C in the presence of 5–10 mol % of CuI and total monomer concentration of 40–50%. During polymerization, the equimolar amount (with respect to Cu(I)) of sodium ascorbate was added at intervals to recover monovalent copper. After completion of the reaction, viscous solution of polymer was diluted with DMSO to 5% and either precipitated with isopropanol or filtered and poured on a warmed glass support to prepare films.

The obtained polymers after precipitation as powders are soluble in aprotic dipolar solvents (DMF, DMSO, and NMP) and water on heating both as sodium salt and in free acid form.

At relatively low values of reduced viscosity (0.4–0.8 dL/g), all the polymers form films removable from support, which can be transformed into acid form upon keeping in a MeOH–HCl mixture (10 : 1, v/v). The linear dimensions of hydrated films of the polymers vary considerably upon keeping in water (by 20–40% depending on temperature and time). This fact can sharply limit the possibility of practical application of PEM in fuel cells. Moreover, films prepared from the linear polytriazoles are insufficiently strong to make membrane–electrode assembly (MEA) that can operate for a long time. Therefore we prepared polytriazole networks based on di- and trifunctional monomers that will show limited swelling in water and may be stronger due to crosslinked structure.

First, we carried out test gelation reactions of different monomers to obtain polytriazole networks in DMSO solution. We noted that solid transparent gel was obtained for 10–15 min at 60–80°C when diazide **1** and triacetylenes **5** and **6** were used, whereas reaction mixture showed no gelation upon heating for several hours in the case of diazide **2**. No strong films were prepared if diazide **2** was used.

To prepare films, a mixture of monomers in molar ratio 1 : 1.5 (in agreement with functionality) was dissolved in DMSO, CuI was added as a catalyst, the mix was poured on a glass support, and the solvent was evaporated at 40°C during 10–20 h. Films prepared by reaction molding on the basis of polymer networks show higher strength as compared with films based on linear polytriazoles. On account of three-dimensional structure, they retain their linear dimensions and become only thicker upon swelling when kept in water. These properties of membranes, along with simple preparation, provide a large advantage for the polytriazole networks obtained in this work in comparison with other types of known polyionomers.

Thus, we obtained, via the reaction of 1,3-dipolar addition, and characterized for the first time the linear and network poly(1,2,3-triazoles) containing sulfonic groups. Films prepared from these polymers are very promising for application as membranes in membrane–electrode assemblies of low-temperature hydrogen and methanol fuel cells.

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