



METAL DERIVATIVES OF SULFONATED POLYPHENYLQUINOXALINE

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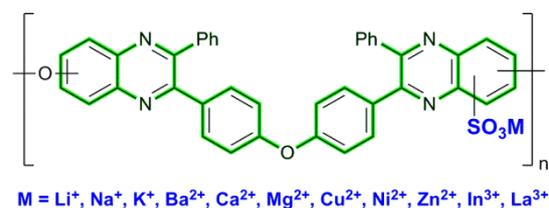
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Abstract

The polymer-analogous transformations of an aromatic ionogenic polymer, namely, sulfonated polyphenylquinoxaline afford a range of polymer salts bearing alkali (Li^+ , Na^+ , K^+), alkaline earth (Mg^{2+} , Ca^{2+} , Ba^{2+}), and transition di- (Cu^{2+} , Ni^{2+} , Zn^{2+}) and trivalent (La^{3+} , In^{3+}) metal ions. The resulting polymers are characterized by elemental and thermogravimetric analyses. The solubility and rheological properties of their dilute and concentrated solutions as well as sensor properties of the coatings based on these polymer salts are explored.



Key words: polyphenylquinoxalines, polymer-analogous reactions, sulfonation, viscosity, ionomers, thermal properties.

Introduction

Sulfonated polyphenylquinoxalines (SPPQs) are of particular interest as the precursors for polyphenylquinoxalines (PPQs) which amount to one of the most promising classes of polyheteroarylenes that combine high thermal and chemical resistance, excellent solubility in organic solvents, and good film-forming properties [1–4].

Experimental

The sulfonated polyphenylquinoxalines were obtained by the polymer-analogous transformations of the PPQs in two steps.

1. First, high-molecular film-forming PPQs fully soluble in chloroform, benzyl alcohol, *N*-methylpyrrolidone (NMP), *m*-cresol, and sulfuric acid were obtained. The reactions were carried out in chloroform at 20 °C using methanol as a proton donor [5].

2. The subsequent sulfonation of the PPQs was accomplished upon treatment with a mixture of sulfuric acid and oleum at 120 °C according to the following procedure.

Oleum was added to a 6% dark-red solution of PPQ in sulfuric acid after cessation of an exothermic reaction in a 4:1 ratio. The reaction mixture was stirred at 120 °C for 10–35 h. The target polymer was precipitated with distilled water, filtered off, rinsed until neutral reaction, extracted with acetone, filtered off again, and dried first in the air and then under vacuum at 50 °C to constant mass. The sulfur content in the resulting samples ranged within 1.7–9.1 wt % [5].

Table 1 presents the conditions for preparation and characteristics of the resulting SPPQs.

The sulfonated PPQs do not dissolve in chloroform; therefore, their films for further studies were prepared from NMP solutions on a horizontal glassy substrate upon heating in argon at 85 °C.

The polymers bearing sulfo groups are conventionally used in the production of ionomers [6, 7]. The presence of SO_3H groups allows for obtaining SPPQ-based polymer salts which properties depend on the type and amount of the introduced cations. The neutralization of sulfo groups with metal ions leads to the formation of ionic pairs which electrostatic interaction, in turn, gives rise to multiplets that serve as physical points of a spatial network [8].

An attractive feature of spatial networks in the ionomers based on SPPQs is an opportunity of realization of a potentially new approach to thermal stabilization of polymer electrolytes at temperatures above 250 °C. It was shown that at these temperatures the interaction of sulfo groups gives rise to intermolecular cross links [5]. The main concept is that blocking of sulfo groups in the resulting physical points can hamper the development of a thermochemical destructive process of the interaction between these groups.

Table 1. Conditions for preparation and characteristics of the resulting sulfonated polyphenylquinoxalines

Sample	Reaction time, h	η_{red} , dL/g ^a	S, wt %
SPPQ-1	10	0.30	1.7
SPPQ-2	15	0.30	2.7
SPPQ-3	20	0.46	3.5
SPPQ-4	25	0.61	4.2
SPPQ-5	30	1.10	5.5
SPPQ-6	35	1.12	9.1

^a η_{red} was measured in NMP at 25 °C at the concentration of 0.5 g/dL.

This work deals with the investigation of the effect of the cation nature in ionomers based on SPPQs on their rheological, thermal, and sensor properties.

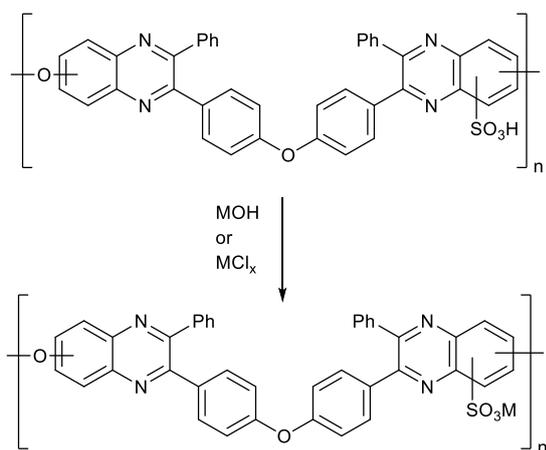
The viscosities of the dilute solutions of the resulting polymers in NMP were defined on an Ubbelohde viscometer with a hanging level in the concentration range of 0.1–1.0 dL/g at 25 ± 0.05 °C. The molar mass of the starting PPQ was determined by the Kuhn–Mark–Houwink equation which parameters were defined earlier [9]. It composed 20 kDa.

The thermogravimetric analysis (TGA) was performed on a Derivatograph-C unit (MOM, Hungary) in the air at the heating rate of 5 °C/min using ~15 mg samples.

The rheological properties of the concentrated polymer solutions were determined on an Anton Paar MCR 302 rheometer (Austria).

The sensor properties of the resulting polymeric materials were explored for potassium salt SPPQ-5-K used as a representative example. The coatings were obtained by electron-beam dispersing of the polymers under vacuum. The coating was applied on a sital substrate with an interdigital microelectrode system. The electrodes were placed on the substrate by photolithography. Their width composed 15 μm , their length was 4 mm; the total amount of the electrodes was 140. The nickel electrodes were applied to the substrate by vacuum deposition. The thickness of the SPPQ-5-K coating according to the results of piezoelectric microweighing studies composed 20 nm. The electroconductivity of the sensor system was measured at an alternating current with the frequency of 1 kHz using a E7-20 immittance meter.

The hydrogen atoms in sulfo groups of SPPQs (featuring different sulfonation degrees) were substituted according to the scheme presented below under heterogeneous conditions using the earlier described procedures [10, 11].



For this purpose, the powders and films of the SPPQs of different compositions were covered with 5M aqueous solutions of alkali metal hydroxides or 10% aqueous solutions of metal chlorides and left at room temperature for 7 days. Then, the resulting polymer salts were thoroughly washed with water until neutral pH and dried in the air at 150 °C to constant mass.

The hydrogen substitution degree in sulfo groups was calculated from the amount of metal introduced into the polymer, which was defined by flame emission spectrometry and/or non-destructive X-ray fluorescence technique.

Results and discussion

A series of the polymeric salts of SPPQs bearing alkali (Li^+ , Na^+ , K^+), alkaline earth (Mg^{2+} , Ca^{2+} , Ba^{2+}), and transition di- (Cu^{2+} , Ni^{2+} , Zn^{2+}) and trivalent (La^{3+} , In^{3+}) metal ions were obtained. Hereinafter, the resulting SPPQ salts will be designated as SPPQ-M, where M is the corresponding cation. The conversion of PPQ to SPPQ is accompanied by significant changes in the physicochemical properties, in particular, solubility. One of the peculiarities of SPPQs and their salts is the high polarity of the main chain and charged side groups. As a consequence, there is only a restricted range of solvents that can dissolve these polymers. The SPPQs bearing over 1.7 wt % of S lose the solubility in chloroform, whereas at the sulfur content over 8.0 wt %, they start to dissolve in ethanol and swell in water.

It was found that common solvents for the PPQ, SPPQs, and their salts with alkali, alkaline earth, and transition di- and trivalent metal ions are aprotic solvents, in particular, NMP.

Furthermore, we revealed a specific feature of the solutions of the SPPQs and their salts in NMP: conversion of the polymers to a water-soluble state *via* gradual replacement of NMP for water. Such a substitution of the solvent was accomplished in the following manner. An NMP solution of SPPQ or its salt (5 wt %) was poured into a dialysis bag which was placed into a vessel with distilled water and kept in it under constant stirring and periodic replacement of water for 10 days. The dialysis and removal of NMP afforded a homogeneous aqueous solution of SPPQ with a polymer concentration of no less than 1 wt %. This unusual phenomenon is of paramount interest from the viewpoint of preparation of aqueous solutions of polymers that cannot be directly dissolved in water.

Rheological properties of the dilute solutions of the SPPQ salts

There are only limited data on the behavior of conventional ionomers in polar solvents due to the restricted solubility of their main, as a rule, nonpolar chain in polar solvents [12, 13]. Nevertheless, the previously obtained results allow for concluding that ionomers undergo partial dissociation in polar solvents that leads to a polyelectrolyte effect.

A criterion for the manifestation of polyelectrolyte or ionomeric properties of the polymers bearing ionogenic sulfo groups and their salts is the characteristic behavior of the reduced viscosity of their dilute solutions. Therefore, we studied the solubility of all the mentioned polymers and measured the concentration dependences of the reduced viscosity in NMP. An increase in the reduced viscosity of the SPPQ solutions in NMP and manifestation of the polyelectrolyte effect with an increase in the sulfonation degree of the initial polymer were observed. The ionomers based on the SPPQs featuring different contents of alkali metals [14] are also soluble in NMP and reveal the polyelectrolyte effect. The higher the metal content, the greater this effect. It should also be noted that the reduced viscosity of the ionomer solutions increased compared to that of the initial sulfonated polymers: this feature is characteristic of the solutions of all ionomers.

In our further studies, we chose the SPPQ bearing 5.5 wt % of sulfur as the main research object.

In the solutions of the SPPQ neutralized with alkaline earth metals, the polyelectrolyte effect almost was not manifested, and the concentration dependences of the reduced viscosity were almost the same and did not depend on the cation type (Fig. 1).

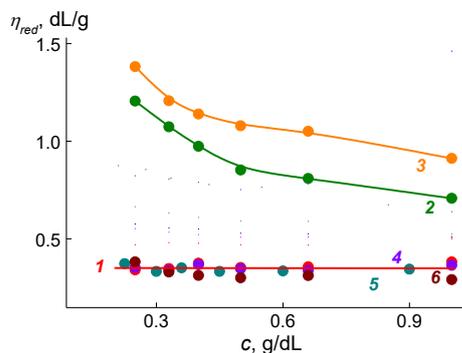


Figure 1. Concentration dependences of the reduced viscosity of the NMP solutions of PPQ (1), SPPQ (2), SPPQ- K^+ (3), SPPQ- Ba^{2+} (4), SPPQ- Ca^{2+} (5), and SPPQ- Mg^{2+} (6).

This surprising fact evidences the suppression of the polyelectrolyte effect upon the introduction of divalent cations into the SPPQ molecules. Moreover, the equality of the reduced viscosities indicates the absence of macromolecular associates in solutions, which could be formed owing to the interaction of ionic pairs. The lack of the polyelectrolyte effect can also be connected with the association of positively charged ions that results, in particular, in the formation of ionic pairs in a nonaqueous solvent. The binding of the ions can be caused by both mere electrostatic attraction of oppositely charged ions and more specific interaction that leads to the formation of ion pairs. The introduction of transition metal cations into the SPPQs, as well as in the previous cases, gives rise to NMP-soluble polymers. Figure 2 presents the concentration dependences of the reduced viscosity of the solutions of SPPQ- Cu^{2+} , SPPQ- Ni^{2+} , and SPPQ- Zn^{2+} .

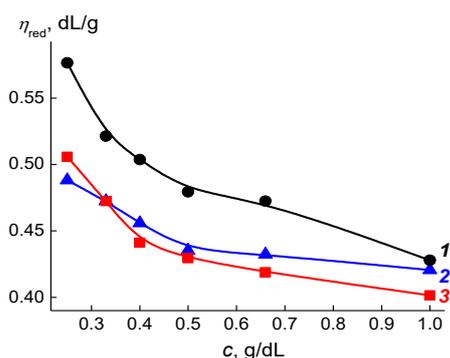


Figure 2. Concentration dependences of the reduced viscosity of the NMP solutions of SPPQ- Cu^{2+} (1), SPPQ- Ni^{2+} (2), and SPPQ- Zn^{2+} (3).

It is obvious that the rheological behavior is similar to that of the solutions of the SPPQ salts bearing alkaline earth metals. Of note is the lower reduced viscosities of the salts containing alkaline earth and transition metal ions compared to the SPPQ and its salts bearing alkaline earth metal ions. The lower reduced viscosity may testify to a denser conformation of a macromolecular coil owing to the intramolecular contacts

between ion pairs or as a result of the realization of other specific interactions.

Rheological properties of the concentrated solutions

The interaction of the SPPQ with trivalent metal salts (In and La) led to the formation of the polymer salts that partially swell in NMP. To compare the rheological behavior of the salt solutions, we studied the viscoelastic properties of their 30% solutions in the mode of sinusoidal oscillations.

Figure 3 presents the frequency dependences of elastic modulus G' and loss modulus G'' for the solutions of SPPQ- La^{3+} and SPPQ- In^{3+} .

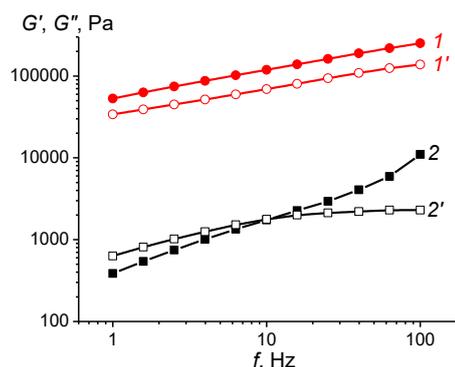


Figure 3. Frequency dependences of G' (1, 2) and G'' (1', 2') for 30 wt % NMP solutions of SPPQ- In^{3+} (1, 1') and SPPQ- La^{3+} (2, 2').

The dependences in Fig. 3 show that the solution of SPPQ- In^{3+} features much higher values of G' and G'' than that of SPPQ- La^{3+} . Furthermore, for the solution of SPPQ- In^{3+} , $G' > G''$ in the whole frequency range, which is characteristic of elastomers. The solution of SPPQ- La^{3+} exhibits the elastomer properties ($G' > G''$) at frequencies above 10 Hz, which is indicative of a relatively mobile fluctuation mesh network that arises at the high frequencies.

The viscosities of the concentrated solutions of the metal-containing SPPQ derivatives were measured in a dynamic mode and are presented in Fig. 4 in the form of the dependences of complex viscosity $[\eta]^*$ on the frequency.

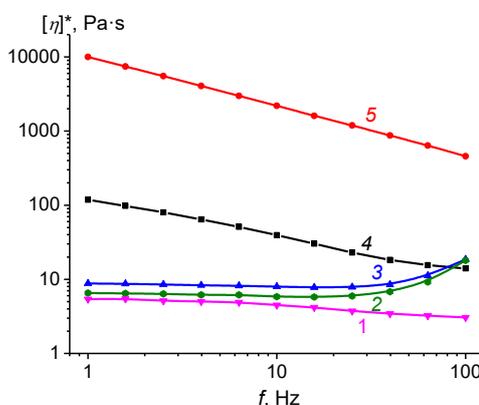


Figure 4. Frequency dependences of $[\eta]^*$ for 30 wt % NMP solutions of SPPQ- Ba^{2+} (1), SPPQ- Zn^{2+} (2), SPPQ- Cu^{2+} (3), SPPQ- La^{3+} (4), and SPPQ- In^{3+} (5).

The resulting dependences suggest that the solutions of the SPPQ neutralized with trivalent metal salts have the highest complex viscosity. The viscosities of the solutions of the SPPQs bearing Cu^{2+} and Zn^{2+} ions at the lower frequencies almost do not differ from each other; the values of their $[\eta]^*$ are considerably lower than those for SPPQ- La^{3+} . Nevertheless, at the higher frequencies, the value of $[\eta]^*$ grows, which is likely to be connected with the realization of fluctuation intermolecular interactions in these solutions. The lowest viscosity was observed for the solution of SPPQ- Ba^{2+} for which $[\eta]^*$ only weakly depended on the frequency.

Thermal properties

Figure 5 demonstrates the thermogravimetric curves for a series of the SPPQs modified with different metal cations.

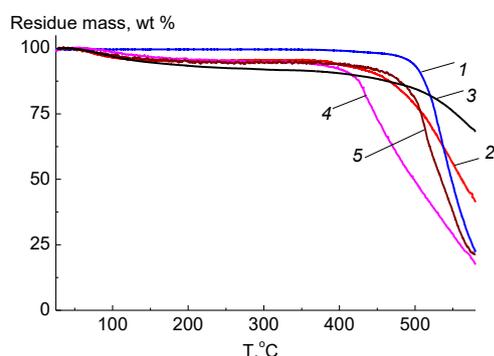


Figure 5. TGA curves for PPQ (1) and SPPQ salts with Na (2), Ca (3), Ni (4), and La (5) ions obtained during heating in the air with the rate of $10\text{ }^\circ\text{C}/\text{min}$.

It is obvious that the introduction of metal ions affects the ability of the resulting ionomers to adsorb moisture from the air (up to 10 wt %). The low-temperature region of the mass loss on the TGA curves in the temperature range of $80\text{--}200\text{ }^\circ\text{C}$ corresponds to the removal of water. The temperatures of decomposition beginning for a whole series of the polymer salts obtained are presented in Table 2. It should be noted that by changing the type of the introduced metal, one can achieve different thermal resistances, in particular, the values close to this parameter for PPQ. This fact implies the possibility of thermal stabilization of polyelectrolytes, at least those with the ionogenic sulfo groups, through their conversion to the corresponding ionomers or polyelectrolytes.

Sensor properties

SPPQs and their salts find application in the production of coatings for electrochemical impedance microsensors [15, 16]. The operating principle of impedance microsensors is based on the definition of a difference in dielectric permeabilities of the liquid medium under consideration and a reference solution, which are contacted with a planar system of microelectrodes covered with different polymeric materials. The use of the SPPQ potassium salt was stipulated by the necessity of the creation of light-targeted potentiometric sensors for biological applications, in particular, for local detection of potassium ions *via* the application of ion-selective coatings [17, 18].

Table 2. Temperature of the decomposition beginning of the resulting polymer salts

Metal	$T_d^{5\%},\text{ }^\circ\text{C}$
Alkali	Li 439
	Na 426
	K 451
Alkaline earth	Mg 410
	Ca 470
	Ba 456
Transition divalent	Ni 415
	Cu 370
	Zn 457
Transition trivalent	In 439
	La 472

It should be noted that electron-beam dispersing of the polymers under vacuum, which was used for the application of the SPPQ-5-K coating, allows one to obtain the coatings with high adhesion to a substrate [19, 20]. It was established that the electroconductivity of the sensors with the coatings in an aqueous solution of potassium chloride increases more than by an order of magnitude compared to distilled water and is twice as much as that in a solution of sodium chloride with the same concentration. The observed difference in the properties shows the great potential of the SPPQ salts in the production of coatings for electrochemical impedance microsensors.

Conclusions

Hence, the introduction of metal cations of different nature into the SPPQs afforded soluble polymer salts that feature high thermal stability. The dilute solutions of alkali and transition metal salts in NMP exhibited polyelectrolyte properties unlike the solutions of the SPPQ salts in which the counter ions were alkaline earth metal cations. The salts of trivalent metals displayed limited solubility. It was found that the dialysis of the NMP solutions of the SPPQ and its salts in water can convert them to a water-soluble form, which opens up new prospects for the use of polymer salts. In addition, the possibility of application of the SPPQ salts as coatings for electrochemical impedance microsensors was demonstrated.

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