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Synthesis and Characterization of the Proton-Conducting Gels Based on PVdF and PMMA Matrixes Doped with Heteropolyacids

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Novel proton-conducting gels have been prepared by entrapping heteropolyacids solutions in polar aprotic solvents within the polymer matrix. The influence of the type of solvent, polymer matrix, and acid concentration on the conductivity, mechanical properties, and thermal stability has been examined. Poly(methyl methacrylate)-based electrolytes show improved optical transparency and mechanical properties in comparison with poly(vinylidene fluoride)-based gels with a slight decrease in the conductivity. The high proton conductivity values in the wide temperature range from 5×10^{-4} S/cm at −60 °C to 8×10^{-3} S/cm at 90 °C make the obtained gels promising materials for application in electrochemical devices. Transport of the proton has also been studied on the basis of the analysis of conductivity data.

1. Introduction

Polymer electrolytes are one of the most widely studied ambient temperature solid ionic conductors because of the possibility of their application in various electrochemical devices, such as batteries, fuel cells, sensors, electrochromic windows, and displays.[1] In recent years growing interest has been focusing on proton-conducting polymer systems mainly based on complexes of electrodonor polymers with strong inorganic acids.[2] Properties of these systems have been described in a recent review.[3] Recently, a new type of proton-conducting system based on polymer gels was developed. Hydrogels[4,5] have been investigated as perspective materials for fuel cells or humidity sensors. Anhydrous systems based on polar aprotic solvents seem to be more suitable for use in devices containing moisture-sensitive materials, such as electrochromic windows. Several types of gels, doped with inorganic[6,7] and organic[8,9] acids, have been investigated to this end. However, their ambient and subambient temperature conductivities are still not high enough for practical application.

The idea of the presented work was to use heteropolyacids (HPA) as proton donors for highly conducting nonaqueous systems. The main goal of our research was to obtain electrolytes combining high conductivity of HPA with processibility of polymer matrixes. Heteropolyacids have been known as materials showing excellent proton conductivity in the crystalline state as well as in water and acetonitrile solution, reaching, for fully hydrated crystals of phosphotungstic acid ($H_3PW_{12}O_{40}\cdot 29H_2O$) and phosphomolybdic acid ($H_3PMo_{12}O_{40}\cdot 29H_2O$), 0.17 and 0.18 S/cm, respectively.[10] So far, most of the investigations have been conducted on solid electrolytes containing HPA supported in either an organic (polymer)[11] or an inorganic (silica)[12] matrix as attractive materials for fuel cells. Our research led us to the conclusion that HPAs are suitable also for use in anhydrous gel electrolytes.

The relationship between the electrolyte composition as well as interactions of electrolyte components have been studied by means of impedance spectroscopy, FT-IR, and DSC methods. The possible mechanism for conductivity is discussed on the basis of the conductivity data.

2. Experimental Section

2.1. Materials. Phosphotungstic acid hydrate ($H_3PW_{12}O_{40}\cdot xH_2O$, PWA) (Aldrich, reagent grade), phosphomolybdic acid hydrate ($H_3PMo_{12}O_{40}\cdot xH_2O$, PMoA) (Aldrich, reagent grade), and silicotungstic acid hydrate ($H_4SiW_{12}O_{40}\cdot xH_2O$, SiWA)

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(Aldrich, reagent grade) were used as received. Methyl methacrylate (MMA) (Aldrich, reagent grade) was distilled over calcium hydroxide under vacuum prior to the reaction. Triethylene glycol dimethacrylate (TEGDM, cross-linking agent) (Aldrich), poly(vinylidene fluoride) (PVdF) (Aldrich), *N*,*N*-dimethyl formamide (DMF) (Aldrich, anhydrous), and propylene carbonate (PC) (Aldrich, anhydrous) were used without further purification. Benzoyl peroxide (BP, free radical polymerization initiator) (Aldrich, 70%) was recrystallized from chloroform and dried at room temperature under vacuum.

2.2. Sample Preparation. PVdF-based gels were obtained by direct dissolution of polymer and HPA in DMF. The calculated amounts of acid (5−12 mass % with respect to the solvent) were placed in small glass bottles and dissolved in DMF. This was followed by the addition of the PVdF; the concentration of polymer with respect to DMF was equal to 18−22 mass %. The systems were heated to 50−60 °C with stirring until the clear solution was formed. The bottles were then cooled, placed in a desiccator, and left for ≈1 week to allow for gelation.

PMMA-based gels were obtained using the following procedure. MMA, TGEDM (3 mass % in polymer matrix), and BP were dissolved in PC placed in a small glass bottle and mixed. The solution was then heated in 75−80 °C for 24 h to allow the polymerization of MMA. After cooling, the resultant gel was soaked with the solution of the selected acid in DMF and left in a desiccator for 1−2 weeks. All operations were performed in a nitrogen-filled drybox (moisture content <2 ppm). Gel electrolytes were obtained for the following components concentration range: 12.5 mass % polymer and 87.5 mass % of the solution of HPA in a solvent mixture consisting of 1 part of DMF and 4 parts of PC with the HPA concentration in these solutions equal to 5 and 15 mass %.

3. Experimental Techniques

3.1. Impedance Spectroscopy. The conductivity was determined using a impedance spectroscopy method in the temperature range 20−90 °C and for selected samples also in the temperature range −60 to +90 °C. The samples were sandwiched between two stainless steel blocking electrodes in a measurement cell and placed in a temperature-controlled thermostat. The experiments were carried out on a Solartron-Schlumberger 1255 impedance analyzer over the frequency range from 1 kHz to 1 MHz.

3.2. DSC Studies. DSC data were obtained in the −150 to +150 °C temperature range using a Perkin−Elmer Pyris 1 scanning calorimeter with a low-temperature measuring head and liquid-nitrogen-cooling element. Samples were loaded into aluminum pans and stabilized by cooling from room temperature to −150 °C. Samples were then heated at a 20 °C/min rate to 150 °C. An empty pan was used as a reference.

3.3. FTIR Spectroscopy. FTIR spectra were recorded on a Perkin−Elmer System 2000 instrument with a resolution of 1 cm^{-1} in the range 4000−500 cm^{-1}. Samples in a form of thin films were sandwiched between two KBr plates and placed in a temperature-controlled cell; the accuracy of the temperature was estimated to be ±1 °C. Spectra of pure HPA were recorded from powdered samples pressed with KBr.

4. Results and Discussion

The transparency of the prepared gels depends on the polymer matrix as well as the kind of solvent. Gels based on PVdF may be obtained in a narrow polymer (18−22 mass %) and acid (5−12 mass %) concentration range. Beyond these limits either the gel does not form or a phase separation is observed. Electrolytes of the higher acid content (10−12 mass%) became dark and brittle during storage. In contrast, the use of PMMA and PC/DMF solvent mixture allowed us to prepare gels of higher (up to 15 mass %) acid concentration, which did not change their properties during 6 months of storage. In comparison with PVdF-based systems the PMMA-containing electrolytes show better mechanical properties and adhesion to the glass substrate. The improvement in transparency results from the fact, that—unlikely to PVdF-based gels—they do not contain crystalline domains.

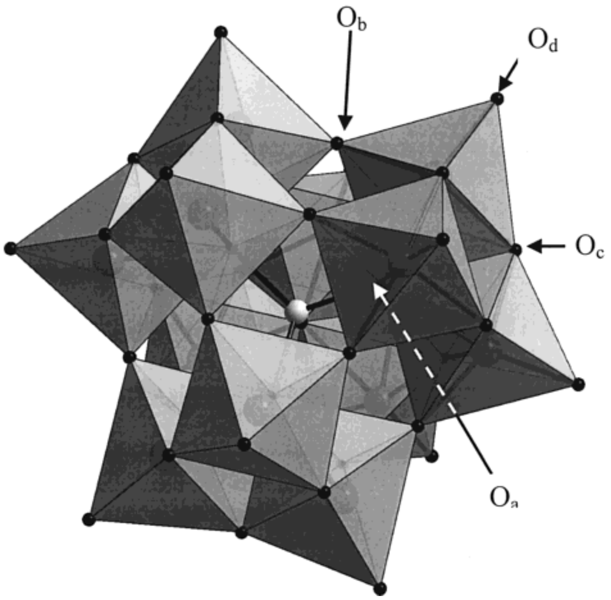

Figure 1. Scheme of the Keggin structure $XM_{12}O_{40}{}^{n-}$. O_a: oxygen atoms connected with MO_4 and XO_4 units; O_b, O_c: bridge oxygen atoms linking MO_4 octahedra from the same (O_c) or different (O_b) M_3O_{13} sets. O_d: external (corner) oxygen atoms.

4.1. FTIR Studies. Anions of heteropolyacids $XM_{12}O_{40}{}^{n-}$ (X = P, Si; M = W, Mo) belong to the Keggin structure.[13,14] Figure 1 presents its schematic representation. The central tetrahedron of $XO_4{}^{n-}$ is surrounded by four sets consisting of three octahedral units of MO_3, which are linked together with oxygen atoms. In the crystalline state the Keggin units are connected in a network thanks to the water molecules and hydrated protons. Therefore, four types of oxygen may be distinguished: O_a, connected with the atoms of M and X; bridge oxygens linking M atoms that belong to different MO_3 sets (O_b) and inside the MO_3 set (O_c); O_d, external O atoms. The IR data for pure HPA and chosen gel compositions are collected in Table 1. The assignment of the bands has been made according to data published by Rocchioli et al.[15]

The positions of vibration modes of all types of M−O bonds are strongly affected by the interactions with neighboring anions and solvent. However, characteristic bands of HPA may be masked by those from the solvent or polymer. It has been assumed that interactions of HPA in polymer gel or acid solutions of the same acid concentration are similar. Therefore, the spectra of HPA-doped gels have been compared with the spectra of pure HPA and of solutions containing 5, 15, and 40 mass % of acid in DMF or a PC/DMF mixture. Figure 2a,b presents exemplary spectra of PVdF−HPA−DMF

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Table 1. Dependencies of the Position of W−O and Mo−O ν_{asym} Characteristic Vibration on the Electrolyte Composition

electrolyte[c]	maximum of the peak (cm^{-1})			
	P−O_a−W	W−O_d−W	W−O_b−W	W−O_c−W
phosphotungstic acid	1080	983	891	802
PWA−DMF solution[a]	1080	979	898	825
PVdF−DMF−PWA gel electrolyte[b]	1079	980	898	825
PMMA−DMF−PC−PWA gel	1080	980	897	824

electrolyte[c]	maximum of the peak (cm^{-1})			
	Si−O_a−W	W−O_d−W	W−O_b−W	W−O_c−W
silicotungstic acid	928	980	880	783
SiWA−DMF solution[a]	922	970	886	808
PVdF−DMF−SiWA gel electrolyte[b]	922	970	881	806
PMMA−DMF−PC−SiWA gel	923	970	885	806

electrolyte[c]	maximum of the peak (cm^{-1})			
	Mo−O_a−Mo	Mo−O_d−Mo	Mo−O_b−Mo	Mo−O_c−Mo
phosphomolybdic acid	1064	962	870	794
PVdF−DMF−PMoA gel electrolyte[b]	masked	959	878	815
PMMA−DMF−PC−PMoA gel	masked	960	878	815

[a] 5 mass % of acid. [b] Samples containing 5 mass % of acid and 18 mass % of polymer in DMF solution. [c] Samples of 5 mass % of acid and 12.5 mass % of polymer and 20 mass % of DMF in the solvent mixture.

gels and HPA−DMF solutions containing 5 mass % of acid in comparison with that of solid HPA.

The vibrations of the central tetrahedron PO_4 can be examined as almost independent from the rest of the anion, whereas those of SiO_4 are mixed with M−O−M vibrations.[15] Hence, the maximum of the M−O_a−X stretching mode for PWA is centered at 1078−1080 cm^{-1} through the entire gels and solution composition range and does not differ from that typical for crystalline PWA. Similar behavior may be expected for PMoA; unfortunately, the Mo−O_a−P peak is completely masked by the bands related to the solvent. In contrast, SiWA-based electrolytes exhibit a small (6 cm^{-1}) shift of the W−O_a−Si band toward lower frequencies, from 928 to 923 cm^{-1}. Positions of all M−O−M vibration modes exhibit shifting either to lower (M−O_d−M) or to higher frequencies (M−O_b−M, M−O_c−M).

The reported changes are most pronounced in the solutions/gels of the lowest acid content. In diluted solution the interactions between acid anions are weaker than those in pure HPA. The increase of the concentration of acid results in weakening of the interactions between the acid anion and solvent and strengthening of those between anions. Therefore, the observed shifting of the M−O characteristic bands is smaller.

Figure 3 presents a comparison of FTIR spectra of SiWA−DMF solutions containing 5, 15, and 40 mass % of acid. The maximum of the W−O_c−W stretching mode peak varies from 782 cm^{-1} reported for pure SiWA to 808 and 803 cm^{-1} for solutions containing 5 and 40 mass % of acid, respectively. A similar effect has been noticed in PWA solutions: the position of the W−O_c−W band shifts from 802 cm^{-1} for pure PWA to 825 and 820 cm^{-1} for 5 and 40 mass % solutions. The spectra of the DMF/PC-containing systems exhibit similar relationships.

The analysis of the IR spectra gives evidence that “intra-” (O_c) and “inter-”(O_b) bridge oxygens participate in the solvent−anion interactions in contrast to the behavior described for solid silica−HPA composites in which the anion interacts with a silica mostly by corner (O_d) oxygens.[12] The decrease in the frequency of M−O_d−M stretching mode could be explained as a consequence of increasing distance between acid anions and “weakening” of the anion structure. Both M−O_b−M and M−O_c−M exhibit opposite behavior probably because of their mixed bending-stretching character.[15] On the other hand, the decreasing of the interactions between anions can result in the strengthening of M−O bonds connecting MO_3 units inside the polyanion.

It may be assumed that interactions between SiWA anions and solvent are slightly stronger than those which take place in PWA and PMoA solutions. The change in the position of the M−O_a band has been found only in SiWA solutions. This can be influenced by the type of the central cation in the Keggin unit.

For previously investigated H_3PO_4-doped gels [6,7] protonation of the carbonyl group of solvent (DMF) has been confirmed. A similar effect should be expected in HPA-doped electrolytes but because of the much lower concentration of protons, even in concentrated HPA solution, the influence of the protonation on the shape of the DMF $\nu_{C=O}$ band is weaker. The position of the $\nu_{C=O}$ characteristic peak is centered at 1669−1670 cm^{-1} for all gel compositions in comparison with 1672 cm^{-1} for pure DMF. Only in solutions containing 40 mass % of acid is the small protonation effect observed and the maximum of the $\nu_{C=O}$ appears at 1667 cm^{-1}.

4.2. DSC Studies. Table 2 presents DSC data of selected polymer gel samples. The only phase transition observed in the −150 to +50 °C temperature range is the glass temperature of the plasticized polymer matrix. Above this temperature a series of peaks appear that may be assigned to the loss of water. The thermal properties of the gels are affected by the sort of solvent and polymer whereas the type of acid seems not to influence the T_g values. The higher T_g values measured for PMMA-based gels are a consequence of higher viscosity of the PC−DMF mixture used as the solvent in comparison with that of pure DMF. It is worth noticing that an increase of acid concentration slightly increases T_g for PMMA−PC−DMF−HPA electrolytes while PVdF−DMF−HPA shows similar T_g values at −135 to −133 °C in the entire acid and polymer

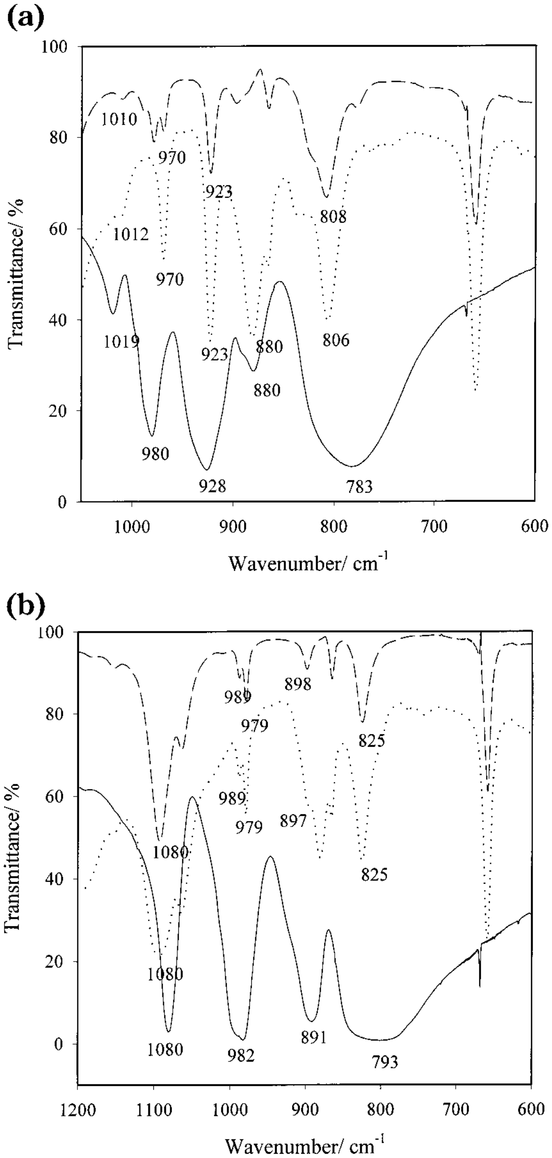

Figure 2. Comparison of FTIR spectra taken for SiWA (a) and PWA (b) and their solutions containing 5 mass % of acid. Solid line, crystalline acid; dashed line and dotted line, DMF solution and PVdF−DMF−HPA electrolytes respectively with acid content equal to 5 mass %.

concentration range. It may be assumed that in both systems the interactions between acid and solvent or polymer, such as formation of hydrogen bonds, should result in stiffening of the gel and increase of the T_g, which has been confirmed for H_3PO_4-doped electrolytes.[6] However, large HPA molecules possess only three (PWA, PMoA) or four protons (SiWA). Thus, the concentration of protons in electrolytes containing 5−15 mass % of HPA is low for all the systems despite the complete dissociation of acid, which results in very similar T_g values for each gel composition.

4.3. Conductivity. The strong acidity of the HPA can be explained as a consequence of the negative charge dispersion over the multiatom polyanion. The external oxygen atoms form a layer that is strongly polarized toward the interior of the complex and present relatively positively charged sides on the outer surface. Therefore, the hydrogen ions are attracted very weakly, which effects their complete dissociation: HPAs are characterized by a p*K* of ≈1.6−2.[16]

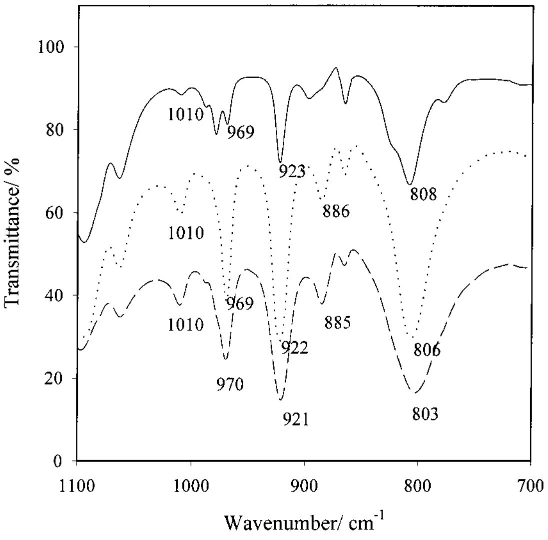

Figure 3. Shift of the maxima of SiWA characteristic vibration modes as a function of acid concentration. The samples contain 5 (solid line), 15 (dotted line), and 40 (dashed line) mass % of acid in the DMF solution.

Table 2. T_g Values of Polymer Gels Doped with Heteropolyacids

samples of the polymer content 12.5 mass % (PMMA) or 18 mass % (PVdF)	acid	concentration of acid/mass %	T_g/°C
PMMA−PC−DMF−HPA[a]	PWA	5	−116
	PMoA	5	−117
	SiWA	5	−117
	SiWA	15	−113
PVdF−DMF−HPA	PWA[b]	5	−134
	PWA	12	−135
	PMoA	12	−135
	SiWA	12	−133

[a] 20 mass % of DMF in a PC/DMF solvent mixture. [b] Sample containing 22 mass % of polymer in DMF solution.

PVdF-Based Gels. Room-temperature conductivities as high as 5 × 10^{-3} S/cm have been achieved. The obtained ionic conductivity values are significantly higher than those reported for H_3PO_4-doped gels[7] and are similar to those for hydrogels.[5] Figure 4a−c presents the relationship between the conductivity and concentration of acid for samples doped with PWA, SiWA, and PMoA of the same polymer content. The conductivity increases with an increase in proton donor content for PMoA and PWA; in the case of SiWA the maximum of the conductivity at 10 mass % of acid is observed.

Figure 5 shows the temperature dependence of the conductivity for PWA- and PMoA-based gels, which is Arrhenius in the entire temperature range, for example, −60 to +90 °C. Low values of activation energies of the range 6−10 kJ/mol calculated on the basis of the following equation,

$$\sigma = \sigma_0 e^{-E_A/(k_B T)}$$

(E_A, activation energy of conduction; k_B, Boltzmann constant; σ_0, pre-exponential factor) indicate a Grotthus-type mechanism of the conduction.[17] The protons can easily protonate DMF molecules, which has been re-

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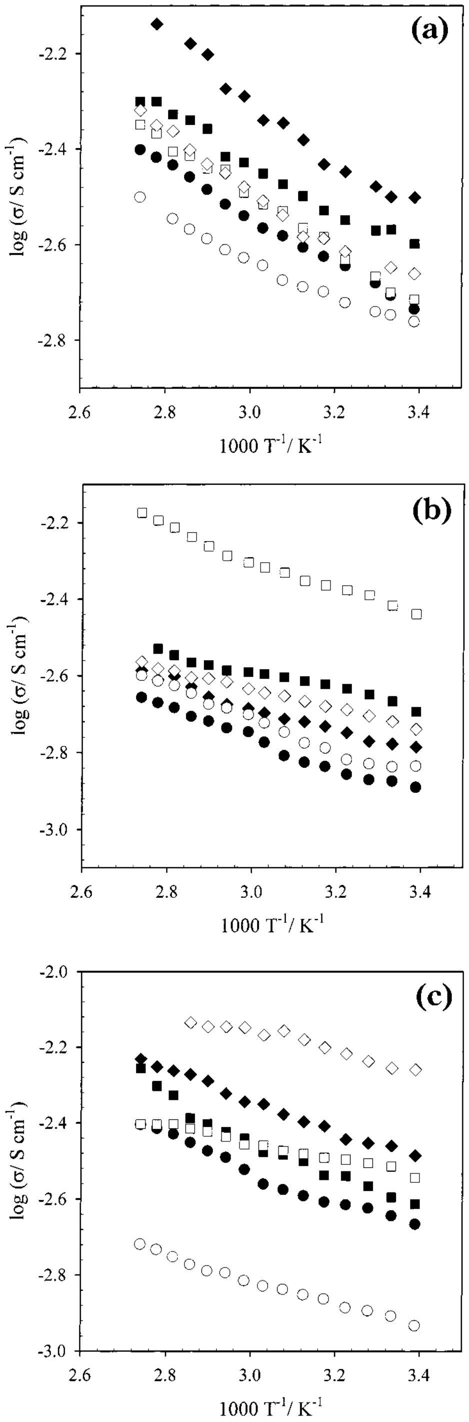

Figure 4. Conductivity as a function of inverse temperature for PVdF–DMF–PWA (a), PVdF–DMF–SiWA (b), and PVdF–DMF–PMoA (c) polymer gels. Systems contain 18 (filled symbols) or 22 (empty symbols) mass % of the polymer in the DMF solutions. Acid concentrations in the DMF solutions equal 5 (○, ●), 10 (□, ■), and 12 (◇, ◆) mass %.

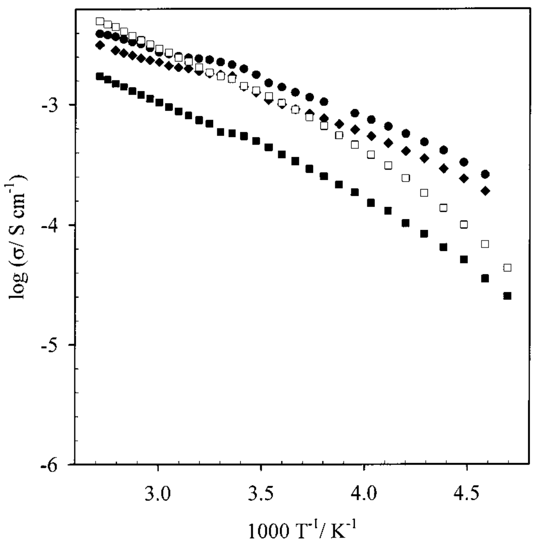

Figure 5. Comparison of the temperature dependence for PMMA- and PVdF-based electrolytes. (●, ◆) PVdF–DMF–PMoA and PVdF–DMF–PWA, respectively, containing 18 mass % of polymer and 5 mass % of acid in DMF solution, (■, □) PMMA–DMF–PC–PWA gel containing 5 and 15 mass % of acid and 12.5 mass % of polymer in the DMF–PC (20% DMF) solvent mixture.

ported in previous work.[6,7] Therefore, the protons can be exchanged between protonated and unprotonated solvent molecules according to the two-step Grotthus mechanism. In the investigated gels an additional effect may be expected: HPA molecules in solution loose a part of the hydratation water that should participate in the exchange of protons. The possibility of a Grotthus-type mechanism of proton conduction has been confirmed by high values of proton diffusion coefficients estimated from electrochemical experiments. Preliminary studies showed that these coefficients are in around 10^{-6} cm^2 s^{-1}.

The lowest activation energies have been found for SiWA electrolytes, which is due to the presence of four acidic protons in SiWA molecules as opposed to three in PMoA and PWA. Among the systems studied, the PMoA-doped samples exhibit the highest conductivities probably because of the higher acidity of pure PMoA in comparison with SiWA and PWA. On the other hand, in gels of the same concentration (in weight %) of PWA and PMoA the molar concentration of protons is higher for PMoA due to its lower molar weight. The substitution of phosphoric acid in a central Keggin unit by silicic acid results in the increase of conductivity, which as mentioned should be explained by the higher number of protons connected with the SiWA molecule.

PMMA-Based Gels. Figure 6 presents the temperature dependence of conductivity for PMMA–PC–DMF–HPA gels electrolytes. The conductivities of these systems at ambient temperatures are similar to those observed for PVdF-based gels but decrease more rapidly with a lowering of temperature. This can be caused either by the protophobic character of PC, which disables the exchange of protons, or its higher viscosity in comparison with that of DMF. The temperature dependence of the conductivity suggests that the proton transport occurs mostly via a Grotthus-type mechanism but the share of the vehicular mechanism, for example, transport of protons as well as with cations H_3O^+ cannot be excluded. This supposition can also be confirmed by higher (15–20 kJ/mol) activation energies of conduction. Similar to the PVdF-based gels, the highest conductivities were obtained for PMoA-based electrolytes. In all the systems studied the conductivity increases with an increase of the acid concentration.

Conclusions

The obtained polymer electrolytes exhibit high conductivity values in the entire temperature range. The

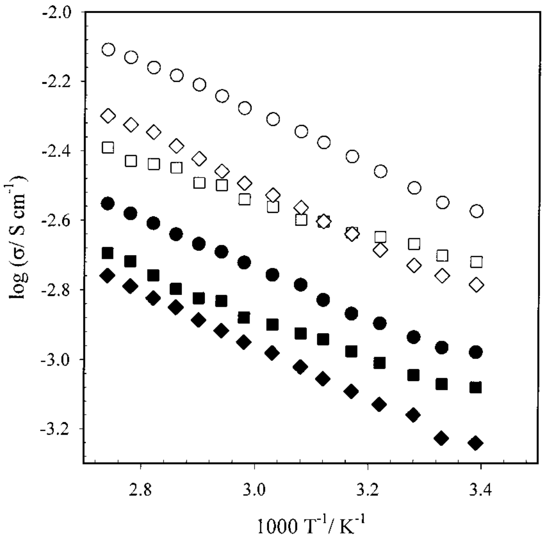

Figure 6. Conductivity as a function of inverse temperature for PMMA−HPA−DMF−PC (20 mass % of DMF in solvent mixture) gels doped with PMoA (○, ●), SiWA (□, ■), and PWA (◇, ◆) containing 12.5 mass % of polymer and 5 (filled symbols) and 15 (empty symbols) mass % of acid, respectively.

analysis of the conductivity data allow us to suspect that the transport of protons occurs via a Grotthus-like mechanism, which is confirmed by the low values of activity energy (<15 kJ/mol) for PVdF−DMF−HPA and PMA−PC−DMF−HPA. It has been shown that PMMA-based gels are characterized by better mechanical properties and enhanced transparency than PVdF-containing gels. The use of PMMA as a polymer matrix allows us to prepare conducting gels in a wider composition range. Among the HPAs tested as dopants, SiWA is the best prospective material for potential applications because of its ability to prepare colorless and transparent gels even at higher acid concentrations, whereas PWA- and PMoA-doped gels become gradually darker. In comparison to previously prepared electrolytes doped with H_3PO_4,[6,7] the described systems exhibit significantly higher conductivities—up to 4 × 10^{-3} S/cm at 25 °C. The preliminary studies of electrochemical stability based on voltammetric experiments show that “stability windows” for SiWA and PWA in DMF solutions are similar to those for H_3PO_4[9] and indicate that HPAs can be useful candidates for application in electrochromic devices.

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