

# Effect of Gel Composition on the Conductivity of Proton-Conducting Gel Polymeric Electrolytes Doped with H<sub>3</sub>PO<sub>4</sub>

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It is shown that the conductivity, mechanical properties, and chemical stability of proton-conducting polymer gel electrolytes based on polymethacrylate matrixes can be modified by changing the polymer matrix composition and accordingly the type and concentration of organic solvent used as plasticizer. The use of the glycidyl methacrylate–methyl methacrylate copolymers enhances ionic conductivity, improves mechanical stability and adhesion to the glass substrate compared to the system based on poly(methyl methacrylate) matrixes, and extends chemical stability compared to the system based on pure poly(glycidyl methacrylate). These copolymers also enable the use of *N,N*-dimethyl formamide–propylene carbonate mixtures as plasticizers, which leads to conductivity enhancement relative to pure propylene carbonate.

## Introduction

Polymer electrolytes doped with proton donors such as strong inorganic acids (H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>) have recently attracted considerable attention due to the possibility of their application in electrochemical devices, like humidity sensors, fuel cells, or electrochromic windows and displays working at ambient and moderate temperatures.<sup>1,2</sup> The variety of systems comprising polymer complexes, polyelectrolytes, and gels have been studied to this end.<sup>1,2</sup>

Recently, several research groups introduced non-aqueous proton-conducting gels as materials for application in electrochromical devices.<sup>3–6</sup> To this end high ionic conductivity, electrochemic and chemical stability, transparency in the visible region, and good mechanical properties and adhesion to the glass substrate are important properties of electrolytes. It has been shown that the properties of the gels studied strongly depend on the type of polymer matrix used as well as the type of solvent and concentration of proton donor.<sup>3</sup> The use of solid organic acids (benzoic acid or salicylic acid) results in the electrolyte conductivity slightly exceeding 10<sup>-4</sup> S/cm at room temperature, which may be too low for practical application.<sup>5,6</sup> On the other hand, the highly

conducting poly(vinylidene fluoride) (PVdF)–*N,N*-dimethylformamide (DMF)–H<sub>3</sub>PO<sub>4</sub> system (room-temperature conductivity approaching 10<sup>-3</sup> S/cm) is transparent in a relatively narrow gel composition range, which is also a serious limitation.<sup>7</sup>

In previous studies one of the highest conductivities, 10<sup>-3</sup> S/cm at ambient temperature, was reported for systems utilizing poly(glycidyl methacrylate) (PGMA) as a polymer matrix.<sup>3</sup> Wider electrochemical, chemical stability, and transparency ranges have been achieved for poly(methyl methacrylate) (PMMA)–propylene carbonate (PC)–H<sub>3</sub>PO<sub>4</sub> gels.<sup>3,4,8</sup> Unfortunately, these systems exhibit much lower conductivities than PGMA–DMF–H<sub>3</sub>PO<sub>4</sub> gels.

The idea of the present work is to combine the good chemical and electrochemical stability and the humidity resistance of PMMA–PC systems with the high conductivity of PGMA–DMF electrolytes. This was realized by the synthesis of glycidyl methacrylate–methyl methacrylate (GMA–MMA) copolymers, prepared by in situ copolymerization in DMF, *N,N*-dimethylacetamide (DMA), and DMF–PC mixtures in the presence of H<sub>3</sub>PO<sub>4</sub>. The physical and chemical properties of these gel electrolytes were examined by the impedance spectroscopy, DSC, and FT-IR techniques.

## Experimental Section

**Materials.** MMA (Aldrich, reagent grade) was distilled over calcium hydroxide under vacuum prior to the reaction. DMA (Aldrich, anhydrous), DMF (Aldrich, anhydrous), PC (Aldrich, anhydrous), and GMA (Aldrich, reagent grade) were used without further purification. Benzoyl peroxide (Aldrich, 70%)

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was recrystallized from chloroform and dried under vacuum.  $\text{H}_3\text{PO}_4$  (Aldrich, 98% crystals) was used as received.

**Sample Preparation.** Nonaqueous protonic gels were prepared in small glass reactors by dissolving  $\text{H}_3\text{PO}_4$  in a solvent (DMF, DMA, or PC) or a mixture of these solvents. Monomers and a free radical initiator (benzoyl peroxide) were then added and the mixture was stirred to obtain a homogeneous solution in a nitrogen-filled drybox (moisture content below 2 ppm). Each of the mixtures was heated at 80 °C for 2–24 h to form a gel.

All of the gels containing 40 mass % of GMA in the polymer matrix were colorless and transparent, independently of the acid concentration and solvent used. The decrease of the GMA content below 40 mass % results in reduced transparency and poorer mechanical properties. At 20 mass % of GMA in a polymer matrix, the obtained gels both in DMF and in DMA were opaque and phase separation was observed.

GMA is a difunctional monomer with a reactive double C=C bond and oxirane ring. It is known that the oxirane ring can react with the P–OH group of the phosphoric acid and its mono- or diesters, leading to the formation of C–OH groups. This is followed by the addition reaction of the oxirane ring with C–OH groups according to the so-called “activated monomer mechanism”,<sup>9,10</sup> which leads to a mixture of phosphorus-containing oligoethers with unsaturated bonds in the side chain.<sup>3</sup> As results from <sup>1</sup>HNMR spectroscopy studies, about 40% of GMA molecules participate in the addition of the P–OH groups of  $\text{H}_3\text{PO}_4$  or its esters and 60% adds to the C–OH groups. In the presence of benzoyl peroxide the oligoethers can polymerize via side chain double bonds, forming cross-linked structures. Further details regarding the formation of GMA-based proton-conducting gels were published elsewhere.<sup>3</sup>

### Experimental Techniques

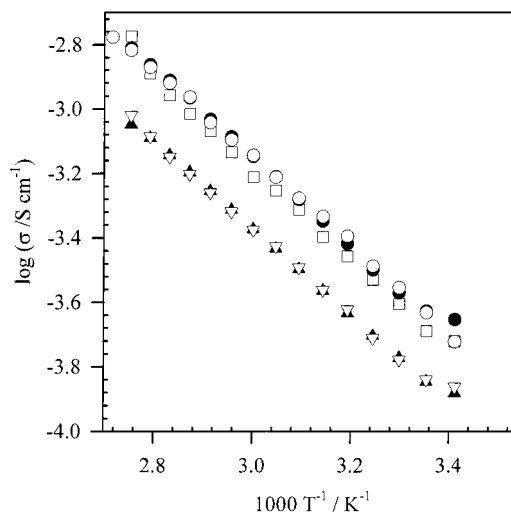
**DSC Studies.** DSC data were obtained between –150 and 150 °C using a Perkin–Elmer Pyris 1 scanning calorimeter with a low-temperature measuring head and liquid-nitrogen-cooled heating element. Samples in aluminum pans were stabilized by slow cooling to –150 °C and then heated at 20 °C/min to 150 °C. An empty aluminum pan was used as a reference.

**Conductivity Measurements.** Ionic conductivity was determined using the complex impedance method in the temperature range from 20 to 90 °C. The samples were sandwiched between stainless steel blocking electrodes and placed in a temperature-controlled oven. The experiments were performed in a constant volume cylindrical cell of the electrode diameter equal to 7.8 mm and fixed electrolytes thickness equal to 1.6 mm. The impedance measurements were carried out on a computer-interfaced Solartron–Schlumberger 1255 impedance analyzer over the frequency range from 1 Hz to 1 MHz.

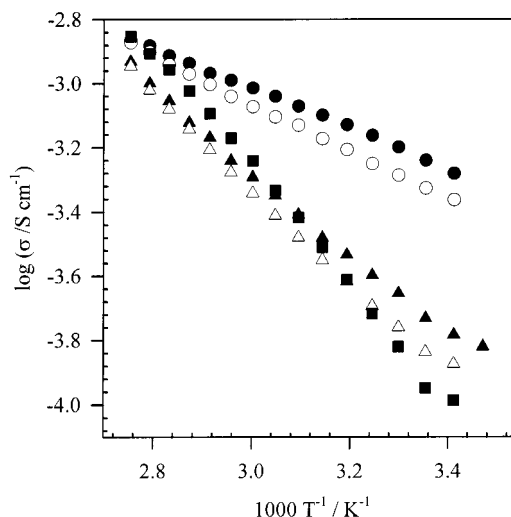
**FT-IR.** Infrared absorption spectra were recorded on a computer-interfaced Perkin–Elmer 2000 FT-IR system with a wavenumber resolution of 1  $\text{cm}^{-1}$ . FT-IR studies were performed at 25 °C. Electrolytes were sandwiched between two NaCl plates and placed in the FT-IR temperature-controlled cell; the accuracy of the temperature was estimated to be  $\pm 1$  °C.

### Results

Figure 1 shows changes in the conductivity of P(MMA-*co*-GMA)–DMF–30%  $\text{H}_3\text{PO}_4$  electrolytes as a function of GMA concentration in the reaction mixture. For samples containing more than 40 mass % of GMA, the conductivities are roughly the same as those for pure



**Figure 1.** Ionic conductivity of the P(GMA-*co*-MMA)–DMF– $\text{H}_3\text{PO}_4$  gel electrolytes as the function of the inverse temperature. All systems contain 12.5 mass % of the polymer matrix and 30 mass % of  $\text{H}_3\text{PO}_4$ . The content of the GMA in the polymer matrix (mass %): (▽) 20, (▲) 30, (□) 40, (●) 50, and (○) 100.



**Figure 2.** Ionic conductivity of the P(GMA-*co*-MMA)–DMF– $\text{H}_3\text{PO}_4$  gel electrolytes as the function of the inverse temperature. All systems contain 12.5 mass % of the polymer matrix with 40 mass % of GMA in it. Concentration of  $\text{H}_3\text{PO}_4$  (mass %): (●) 5, (○) 15, (▲) 25, (△) 30, and (■) 40.

GMA-based gels but conductivities decrease for systems containing less GMA.

Figure 2 shows changes in the conductivity of P(MMA-*co*-GMA)–DMF– $\text{H}_3\text{PO}_4$  gels (with 40 mass % of GMA in the polymer matrix) as a function of  $\text{H}_3\text{PO}_4$  concentration. Ambient temperature conductivities decrease with an increase in the acid concentration and are relatively higher for gels containing 5 and 15 mass % of  $\text{H}_3\text{PO}_4$  than for other systems studied. The activation energy for conduction obtained for these two electrolytes is much lower than those for other systems displayed (see data included in Table 1).

Figure 3 presents the changes in the conductivity of P(MMA-*co*-GMA)–DMA– $\text{H}_3\text{PO}_4$  (40 mass % of GMA) gels as a function of  $\text{H}_3\text{PO}_4$  concentration. The trends shown are similar to those presented in Figure 2. However, ambient temperature conductivities for gels of the lowest  $\text{H}_3\text{PO}_4$  concentration are slightly lower

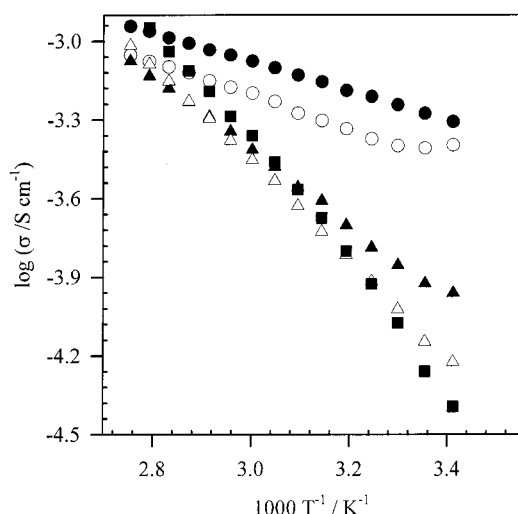
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**Table 1. Activation Energies Calculated by Fitting Experimental Data Obtained for P(GMA-*co*-MMA)-Based Gels to Eq 1**

GMA content in the polymer matrix (mass %)	H <sub>3</sub> PO <sub>4</sub> concentration (mass %)	E <sub>a</sub> (kJ mol <sup>-1</sup> )
P(GMA- <i>co</i> -MMA)-DMF-H <sub>3</sub> PO <sub>4</sub>		
40	5	11.9
40	15	14.2
40	30	27.5
40	40	34.5
20	30	25.2
100	30	25.9
P(GMA- <i>co</i> -MMA)-DMA-H <sub>3</sub> PO <sub>4</sub>		
40	5	10.6
40	40	44.2
P(GMA- <i>co</i> -MMA)-DMF-PC-H <sub>3</sub> PO <sub>4</sub>		
40	5 <sup>a</sup>	13.5
40	30 <sup>a</sup>	28.0
40	5 <sup>b</sup>	11.2
40	30 <sup>b</sup>	25.3

<sup>a</sup> 20 vol % of DMF in the solvent mixture. <sup>b</sup> 60 vol % of DMF in the solvent mixture.



**Figure 3.** Ionic conductivity of the P(GMA-*co*-MMA)-DMA-H<sub>3</sub>PO<sub>4</sub> gel electrolytes as the function of the inverse temperature. All systems contain 12.5 mass % of the polymer matrix with 40 mass % of GMA in it. Concentration of H<sub>3</sub>PO<sub>4</sub> (mass %): (●) 5, (○) 10, (▲) 25, (△) 30, and (■) 40.

than those of analogue systems plasticized with DMF.

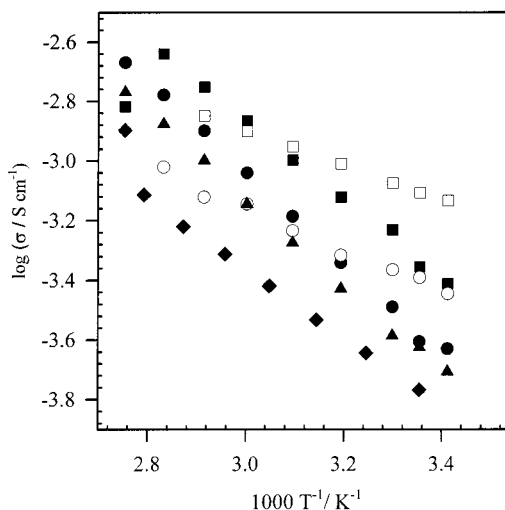
Figure 4 presents the effect of the PC-DMF solvent mixture on the conductivity of GMA (40 mass %)-*co*-MMA-based gel electrolytes. The highest ambient temperature conductivities were achieved for a sample containing 60 mass % of DMF and 30 mass % of H<sub>3</sub>PO<sub>4</sub> and for another sample: 60 mass % of DMF/5 mass % of H<sub>3</sub>PO<sub>4</sub>. The activation energy of the latter is however much lower (see Table 1). Conductivities of samples containing a solvent mixture are generally higher than those for analogue gels plasticized with one solvent.

Most of the systems studied display an Arrhenius type of the temperature dependence of ionic conductivity described by eq 1:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{k_B T}\right) \quad (1)$$

Here,  $E_a$  is an activation energy for conduction,  $\sigma_0$  is a pre-exponential factor, and  $k_B$  is the Boltzmann constant.

Table 1 summarizes the activation energy for conduction determined by the fitting of the experimental data



**Figure 4.** Influence of the solvent composition on the ionic conductivity of the P(GMA-*co*-MMA)-DMF-PC-H<sub>3</sub>PO<sub>4</sub> gels. All systems contain 12.5 mass % of the polymer matrix with 40 mass % of GMA in it. Samples with 30 mass % (filled symbols) and 5 mass % of acid (open symbols), respectively: (●, ○) 20 mass %, (▲) 40 mass %, (■, □) 60 mass %, and (◆) 80 mass % of DMF in the solvent composition.

**Table 2. T<sub>g</sub> Values Measured for P(GMA-*co*-MMA)-Based Electrolytes**

GMA content in the polymer matrix (mass %)	H <sub>3</sub> PO <sub>4</sub> concentration (mass %)	T <sub>g</sub> (°C)
P(MMA- <i>co</i> -GMA)-DMF-H <sub>3</sub> PO <sub>4</sub>		
40	5	-120
40	30	-89
40	40	-73
100	30	-89
P(MMA- <i>co</i> -GMA)-DMF-PC-H <sub>3</sub> PO <sub>4</sub>		
40	5 <sup>a</sup>	-118
40	30 <sup>a</sup>	-86
40	5 <sup>b</sup>	-124
40	30 <sup>b</sup>	-56

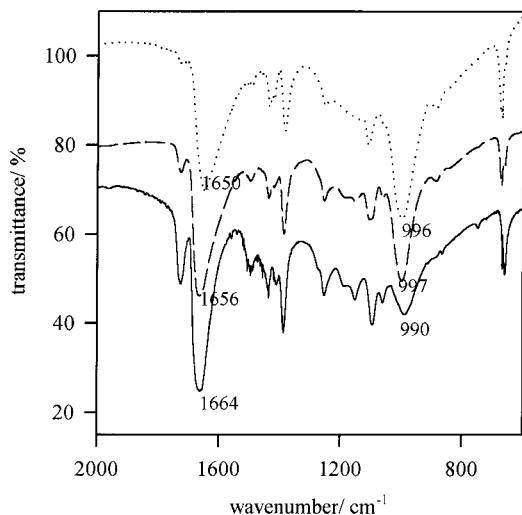
<sup>a</sup> 20 vol % of DMF in the solvent mixture. <sup>b</sup> 60 vol % of DMF in the solvent mixture.

to eq 1. Activation energies increase with an increase in H<sub>3</sub>PO<sub>4</sub> concentration for samples plasticized with DMF or DMA and are weakly dependent on the polymer matrix composition. The use of a (PC + DMF) mixture does not change the activation energies, which are similar to those calculated for samples of the same composition plasticized only with DMF.

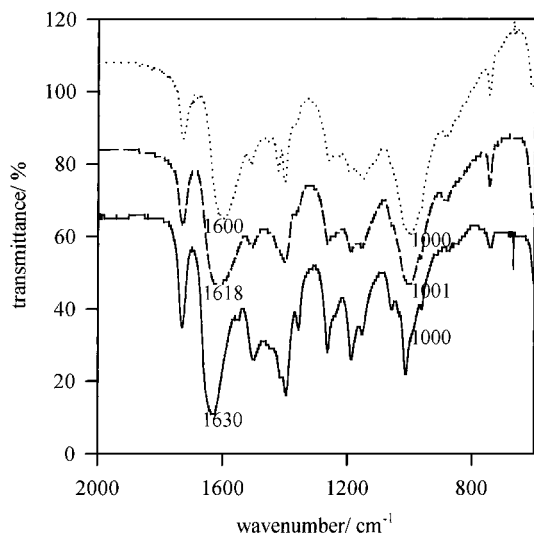
DSC traces of the protonic gels reveal that the only glass transition is in the low-temperature region. Around 100 °C the evaporation of solvent occurs, which limits thermal stability of gel electrolytes. Table 2 presents T<sub>g</sub> values for gel electrolytes. It is shown that T<sub>g</sub> depends strongly on the acid concentration and it decreases with a decrease in the acid concentration for samples of the same polymer matrix and solvent content.

Figures 5 and 6 present FT-IR spectra of the protonic gels plasticized with DMF (Figure 5) and DMA (Figure 6). Two regions characteristic of the ν<sub>C=O</sub> mode of the plasticizer are present around 1700–1600 cm<sup>-1</sup> and the ν<sub>P-O</sub> mode is observed at around 1000 cm<sup>-1</sup>. Both regions are of interest for studies of proton transport mechanisms.<sup>11–13</sup> Table 3 presents the position of

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**Figure 5.** Exemplary FT-IR spectrum measured at 25 °C for P(GMA-co-MMA)-DMF-H<sub>3</sub>PO<sub>4</sub> polymer gels. All samples contain 12.5 mass % of polymer with 40 mass % of GMA in it. Solid line, 5 mass % of H<sub>3</sub>PO<sub>4</sub>; dashed line, 30 mass % of H<sub>3</sub>PO<sub>4</sub>; dotted line, 40 mass % of H<sub>3</sub>PO<sub>4</sub>.



**Figure 6.** Exemplary FT-IR spectrum measured at 25 °C for P(GMA-co-MMA)-DMA-H<sub>3</sub>PO<sub>4</sub> polymer gels. All samples contain 12.5 mass % of polymer with 40 mass % of GMA in it. Solid line, 5 mass % of H<sub>3</sub>PO<sub>4</sub>; dashed line, 30 mass % of H<sub>3</sub>PO<sub>4</sub>; dotted line, 40 mass % of H<sub>3</sub>PO<sub>4</sub>.

characteristic IR modes as a function of gel composition. The position of  $\nu_{\text{C=O}}$  (DMF, DMA) mode shifts to lower wavenumbers with an increase in acid concentration (see also Figures 5 and 6), whereas the position of the  $\nu_{\text{C=O}}$  (PC) mode is almost independent of the amount of acid used. The position of the  $\nu_{\text{P-O}}$  mode weakly depends on the sample composition (see also Figures 5 and 6).

### Discussion

It has been shown that the physical-chemical properties of proton-conducting gels can be easily modified by changes in the composition of a polymeric matrix and type of solvent used to plasticize it. The preparation of

**Table 3.** Position of the Maxima of the Characteristic Bands Measured for P(GMA-co-MMA)-Based Proton-Conducting Gel Electrolytes

mass % of GMA in the polymer matrix	mass % of H <sub>3</sub> PO <sub>4</sub> in the polymer electrolyte	$\nu_{\text{C=O}}$ (cm <sup>-1</sup> )	$\nu_{\text{P-O}}$ (cm <sup>-1</sup> )
P(MMA-co-GMA)-DMF-H <sub>3</sub> PO <sub>4</sub>			
40	5	1664	998
40	15	1660	996
40	30	1657	997
40	40	1652	999
20	30	1654	998
100	30	1652	998
P(MMA-co-GMA)-DMA-H <sub>3</sub> PO <sub>4</sub>			
40	5	1630	1000
40	30	1606	998
40	40	1600	1000
100	30	1601	1001

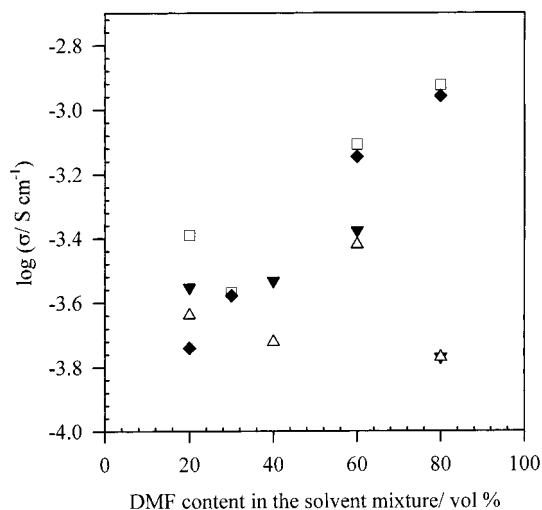
GMA-MMA copolymers enable us to combine the benefits of high conductivity of GMA-based gels with extended chemical and electrochemical stability ranges thanks to the presence of MMA segments and the PC used as the plasticizer. The conductivities measured for copolymer-based gels plasticized with DMF or DMA are comparable to that previously obtained for systems based on pure GMA matrixes.<sup>3</sup> The addition of DMF results in an increase in conductivity compared to pure GMA- or MMA-based electrolytes of the same composition, when the pure PC was used as a plasticizer. The presence of even a small amount of DMF in the solvent mixture results in a conductivity mechanism that is different from that previously suggested for MMA-PC<sup>3</sup>-based electrolytes (see also the activation energies in Table 1). As shown from FT-IR experiments both DMA or (and) DMF carbonyl group can be easily protonated by H<sub>3</sub>PO<sub>4</sub>. This is evident by the decrease of the  $\nu_{\text{C=O}}$  mode with an increase in the H<sub>3</sub>PO<sub>4</sub> concentration. The Arrhenius type of the temperature dependence of conductivity shown in Figure 4 associated with low activation energy values (see Table 1) suggest Grotthus-like proton conduction with the exchange of protons between protonated and unprotonated DMF (DMA) molecules.<sup>3,1514,15</sup> According to a recent review paper,<sup>14</sup> the formation of long pathways between protonated solvent molecules, which is the case for gels based on DMF (DMA), is an indication of the Grotthus-type conduction. Therefore, relatively high ambient temperature conductivities measured for a sample containing 5 mass % of H<sub>3</sub>PO<sub>4</sub> are not surprising. The proton conduction mechanism appears to change with an increase in the H<sub>3</sub>PO<sub>4</sub> concentration, which is indicated by an increase in the activation energy for conduction (see Table 1), suggesting that for samples of the high H<sub>3</sub>PO<sub>4</sub> concentration the vehicle type mechanism dominates or that there is a mixture of both Grotthus- and vehicle-type proton conduction.<sup>15</sup> The addition of even a small amount of DMF caused changes in the conduction mechanism from the vehicle mechanism previously found for samples plasticized with PC<sup>3</sup> to the Grotthus-type mechanism for low acid concentration (associated with low activation energies) or a mixed one for higher acid concentrations (higher activation energies are observed).

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**Figure 7.** Comparison of the conductivity isotherms measured at 25 °C for P(GMA-*co*-MMA)–DMF/PC–H<sub>3</sub>PO<sub>4</sub> gel electrolytes (open symbols) as a function of gel composition with model data (filled symbols) calculated on the basis of an EMT approach (see eq 2). Samples containing 5 mass % (□, ◆) and 30 mass % of acid (▽, ▲).

The above ideas are supported by PFG NMR studies showing a higher diffusion coefficient for DMA-based gels<sup>8</sup> than for PC-based electrolytes.<sup>17</sup> PFG NMR experiments also show a decrease in the proton diffusion coefficient with an increase in the H<sub>3</sub>PO<sub>4</sub> concentration.<sup>16</sup>

The good mechanical properties of samples having low acid concentrations are in good agreement with data obtained for proton-conducting hydrogels as well as the trends described in a recent review paper.<sup>17,18</sup>

Figure 7 shows a comparison of room-temperature conductivities measured for GMA-*co*-MMA–H<sub>3</sub>PO<sub>4</sub> gels plasticized with a PC–DMF mixture with the data calculated using the effective medium theory (EMT), assuming the Bruggeman model.<sup>19</sup> A similar procedure has been previously successfully used to model the conductivity of acrylamide–H<sub>3</sub>PO<sub>4</sub> hydrogels.<sup>20</sup> The assumptions of the model used in the present case are as follows.

For the need of the modeling procedure we have assumed that our gel is a mixture of two phases. These are a PC/acid solution trapped in PMMA (poor conducting phase) and a DMF/acid solution trapped in a PGMA phase (highly conducting phase) and the possibility of the formation of highly conducting pathways through protonated and unprotonated DMF molecules. The bulk conductivity of gels results from interactions between these two phases. Therefore, it seems to be reasonable to apply the EMT to describe the conductivity–DMF concentration isotherm presented in Figure 7. To make these calculations easier, we have assumed that each of the phases mentioned above has spherical symmetry. Under these assumptions each phase in the heteroge-

neous gel material is symmetrically embedded in a self-consistent effective medium with the same effective conductivity  $\sigma^*$  as the bulk gel electrolyte. Our description is thus given in terms of the complex conductivity of this inhomogeneous dielectric material considered to possess macroscopic uniformity. The general self-consistent equation for the multiphase material is

$$\sum_i w_i \frac{\sigma_i - \sigma^*}{\sigma_i + (d-1)\sigma^*} = 0 \quad (2)$$

Here,  $d$  is a dimensionality parameter equal to 3 for spherical aggregates,  $\sigma_i$  ( $i = 1, 2$ ) are conductivities of the PC/H<sub>3</sub>PO<sub>4</sub>/PMMA phase ( $\sigma_1$ ) and DMF/H<sub>3</sub>PO<sub>4</sub>/PGMA phase ( $\sigma_2$ ), and  $w_i$  is the volume fraction of the  $i$ th phase.

As can be seen from Figure 7, the experimental and theoretical data are in good agreement. The same procedure can be used to calculate the changes in the conductivity for other compositions of polymer matrixes.

Because of the presence of GMA segments, which themselves exhibit lower  $T_g$  values than pure PMMA, the flexibility of the obtained gels is higher than that for PMMA-based systems. This conclusion is supported by the DSC experiments, showing low  $T_g$  values of gel electrolytes based on GMA–MMA copolymers. Also, the adhesion of these gels to the glass substrate is better than that for PMMA-based systems because of the presence of polar epoxy groups in the GMA chains. On the other hand, PMMA segments are responsible for the chemical stability against the traces of moisture observed after exposure of the samples to open air. These samples exhibit a much wider transparency range than the GMA-based gels, which become slightly yellowish after a long time in storage. The latter properties are also connected with a large fraction of PC used as a plasticizer. The presence of DMF results in higher water affinity of the gel electrolytes and most probably also affect the transparency of gels.

## Conclusions

It has been shown that the properties of proton-conducting gel electrolytes can be modified by changes in the composition of the polymer matrix and accordingly the plasticizer used and fraction of H<sub>3</sub>PO<sub>4</sub>. Utilization of GMA–MMA copolymers leads to an increase in the conductivity (up to  $\sim 10^{-3}$  S/cm at room temperature) compared to that of pure PMMA-based systems as well as to an improvement in the mechanical properties and adhesion to the glass substrate. The reduction in the fraction of DMF used extends the transparency range of the electrolyte studied compared to a previously used system based on pure poly(glycidyl methacrylate) (PGMA) and improves the resistance toward the traces of moisture. The relation between the composition of gels studied and their conductivity can be predicted by means of effective medium theory procedures.

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