Supplementary Information:

^{1}H DQ Sideband-Patterns:

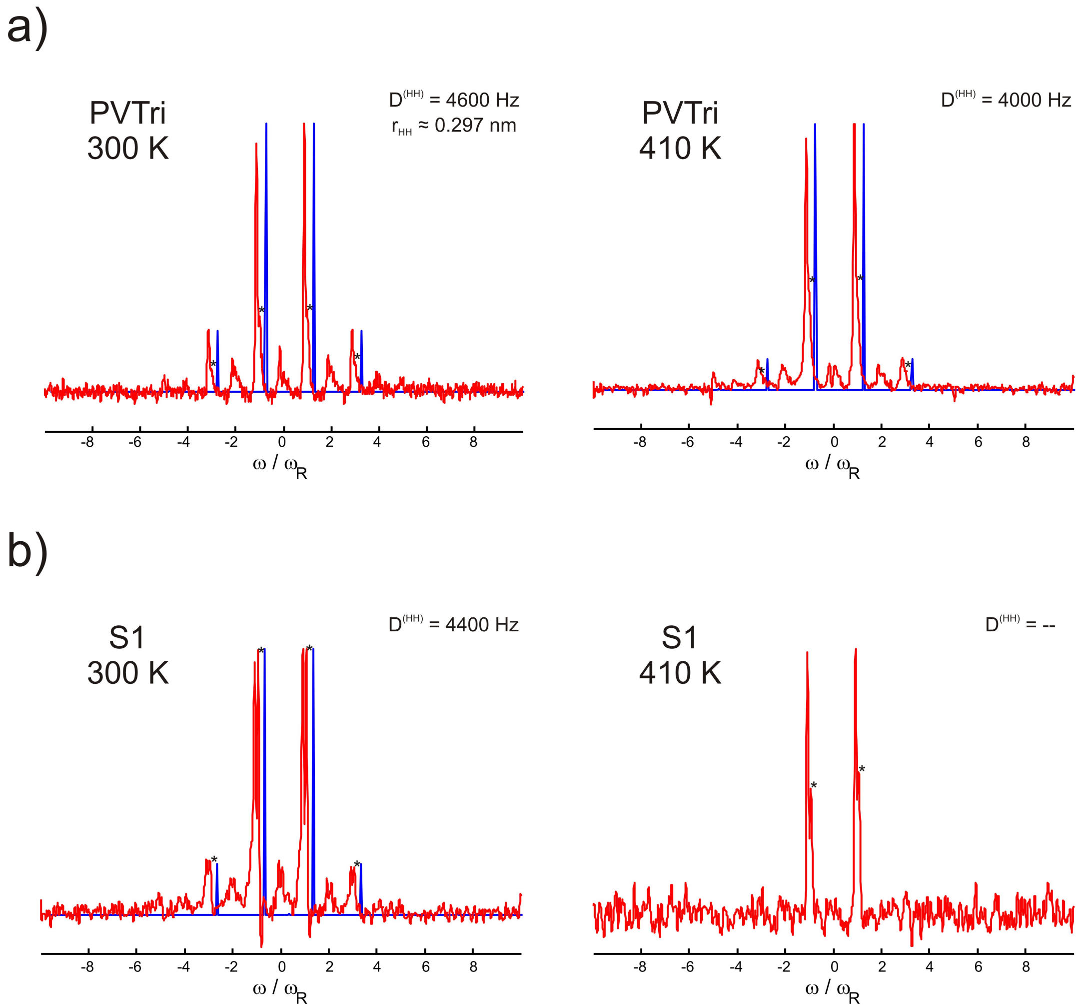

Figure S1: Extracted columns (red) from ^{1}H DQ sideband-pattern MAS spectra of PVTri homopolymer and S1 copolymer recorded at 300 K and 410 K at ~7.8 ppm (corresponds to the chemical shift of the ring CH). In each spectrum, the bets-fit spectrum (blue) is additionally included to the right side of the spectra which was generated by assuming an isolated spin-pair. The resonances marked by * correspond to DQCs between the ring CH protons and other nearby protons. The calculated dipolar couplings and resulting proton distances are included on top right of each spectrum.

^{1}H DQ MAS spinning-sideband-patterns[1] were recorded at 700.1 MHz ^{1}H Larmor frequency with 25 kHz MAS at T=300 and T=410 K. For double-quantum excitation and reconversion the BaBa pulse sequence[2] was applied for four rotor periods. Each of the 512 t_1 increments has been aquired with 32 transients and a relaxation delay of 2 s.

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[*] Corresponding authors. Fax: +90-212-8663402 and +49-6131-379100
e-mail addresses: bozkurt@fatih.edu.tr, and spiess@mpip-mainz.mpg.de
This article is prepared with the equal contributions of both institutions.

Since the observed sideband pattern depends only on the product of the excitation/reconversion time and the dipolar coupling and the MAS spinning frequency, the analysis of these patterns provides the dipolar coupling constant. In rigid spin systems, this coupling constant can be converted into distance information[3].

While the fitted spectra are based on two-spin computations and therefore show only odd-order spinning sidebands, the recorded sideband pattern in Figure S1 have even-order sidebands of significant intensity. These even-order sidebands originate from multi spin effects, which are neglected analyzing the sideband patterns. However, previous studies demonstrated that this approximation is still valid, if the DQ recoupling time is not too long and the MAS spinning frequency is high[3-5]. Moreover, DQ coherences between Tri-CH protons and nearby aliphatic protons are observed in the recorded pattern as a shoulder (marked by *) on the right side of the analysed Tri-CH auto peak pattern.

The dipolar couplings given in Figure S1 are determined in the two spin approximation fitting only intensities of odd-order sidebands in the ^{1}H DQ MAS spectra. For PVTri at 300 K, a dipolar-coupling of 4600 Hz was extracted, which corresponds in a rigid spin system to a distance of ~0.30 nm between neighboring CH protons. Since the distance between Tri-CH protons in the same ring (~0.41 nm) is bigger, the observed Tri-CH DQ coherences have to result from spatial proximities between neighboring triazole rings. At T = 410 K, the dipolar coupling is reduced to 4000 Hz due to an increased mobility of the triazole rings. For the S1 copolymer, at 300 K, the third order sidebands are slightly reduced and a dipolar coupling of 4400 Hz was determined. It should be noted that the DQ coherences between the Tri-CH and the aliphatic protons is much more pronounced in this sample. Moreover, the third order sidebands are not observed at T = 410 K indicating that the dipolar coupling of the copolymer is clearly reduced and cannot be determined with the given experimental settings.

FT-IR Results:

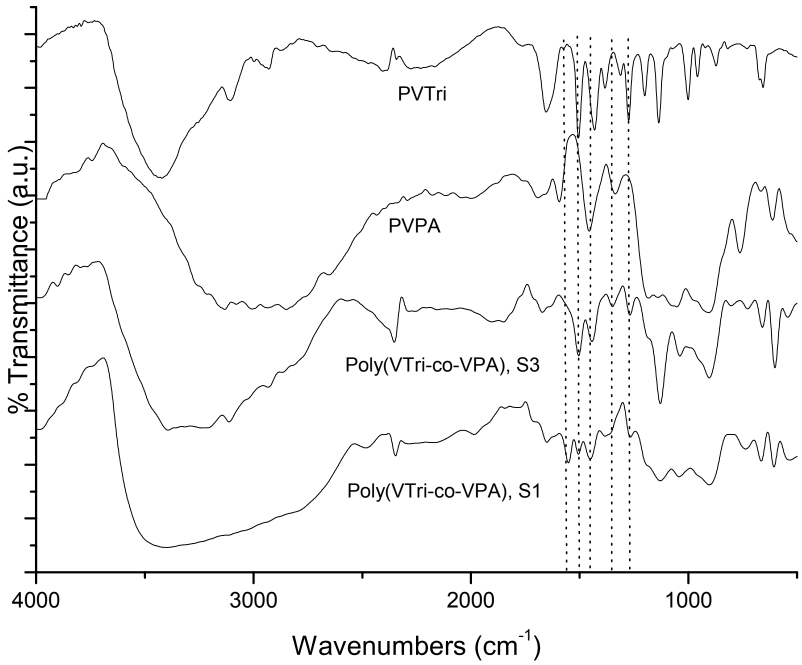

Figure S2: FT-IR spectra of the PVTri, PVPA and the copolymer electrolytes, **S1** and **S3**.

Figure S2 shows the FT-IR spectra of poly(1-vinyl-1,2,4-Triazole), PVTri, polyvinylphosphonic acid, PVPA and the copolymers. In PVTri, the triazole units show several medium or strong bands in the 1430-1650 cm^{-1} range due to ring stretching (C-N, C=N) vibrations. The band at 1270 cm^{-1} is due to the ring N-N stretching. The IR spectrum of PVPA shows strong bands at 1040-910 cm^{-1} that belong to asymmetric stretching vibrations of the P-OH group and at 1150 cm^{-1} that corresponds to P=O stretching.[5] Additionally, phosphonic acid units give rise to broad bands with medium intensity at 1700-1590 cm^{-1} and 2850-2750 cm^{-1}. In the copolymer samples a very strong interaction between phosphonic acid and triazole units can be observed in the fingerprint region. The protonation of the ‘free’ nitrogens of the triazole rings can be observed with the large change of the intensity of the band at 1650 cm^{-1}. Additionally, one can notice the increasing intensity of the near at 910 cm^{-}

^{1} relating to the P-O$^-$ formation for the sample **S3**. The FT-IR data indicate that protonation occurs through transfer of protons from phosphonic acid units to heterocyclic rings to form triazolium ions. The broad band between 3500 cm^{-1}- 2500 cm^{-1} is the hydrogen bonding network which is necessary for proton conduction.

^{31}P MAS NMR Results:

^{31}P MAS NMR spectra of the samples are shown in Figure S3. In the spectra of the dry as-synthesized copolymers the signal of phosphonic acid anhydride is not resolved. However, the asymmetry of the resonances implies indeed the formation of phosphonic acid anhydride.[6] From a deconvolution of the resonances, which was performed using the DMFIT program package,[7] the amount of the different phosphorous sites can be quantified. Before annealing a fraction of ~ 30-40% phosphonic acid anhydride is found in the samples, which increases after annealing up to ~60%. Similar fractions of anhydrate formation have been reported before for pure PVPA.[6] The anhydride formation hampers proton conduction as they block the proton transport pathways for Grotthus-type mechanisms. It seems that copolymerization of PVPA and PVTri does not reduce the anhydride formation. After annealing the copolymers 160°C for 10-12 hours, the anhydride signal (at ~22 ppm) becomes the dominating signal of the ^{31}P spectra. At higher temperatures (above 160°C), the condensation process is even more pronounced, as indicated by the weight loss observed in TGA (shown in Figure S4). NMR experiments at higher temperatures could not be performed due to the instrumental limitations.

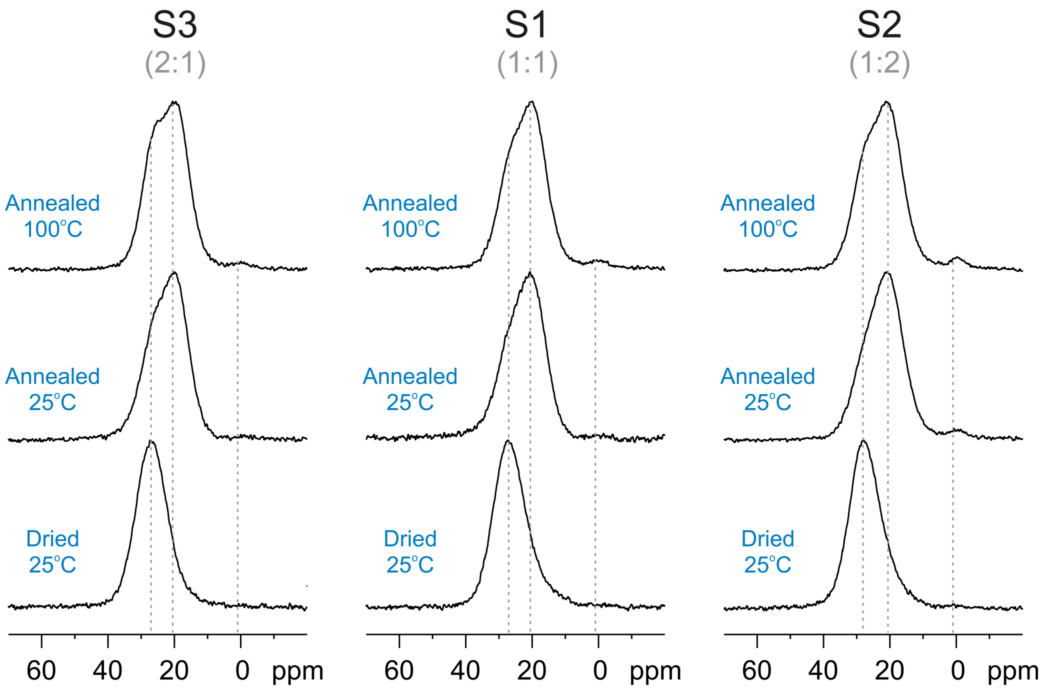

Figure S3: ^{31}P MAS NMR spectra of the annealed and the non-annealed dried copolymer, **S1**, **S2**, and **S3** recorded at 25°C and 100°C. The spectra recorded at 283.42 MHz ^{31}P Larmor frequency and at 25 kHz MAS frequency. The procedures of annealing and drying are explained in the text. A relaxation delay of 5 seconds was used in the single-pulse experiment.

The weak resonance observed at ~0-2 ppm in annealed materials is assigned to phosphonic acid groups cleaved from the polymer backbone. This cleavage process appears only after intense annealing for several hours and is rather weak as indicated by the low intensity of this resonance (~1-3%).

Thermal Properties :

Figure S4 shows the thermogravimetry results of the homopolymer, PVTri and the copolymer, S2 at a heating rate of 10 °C/min. The homopolymer PVTri has considerable

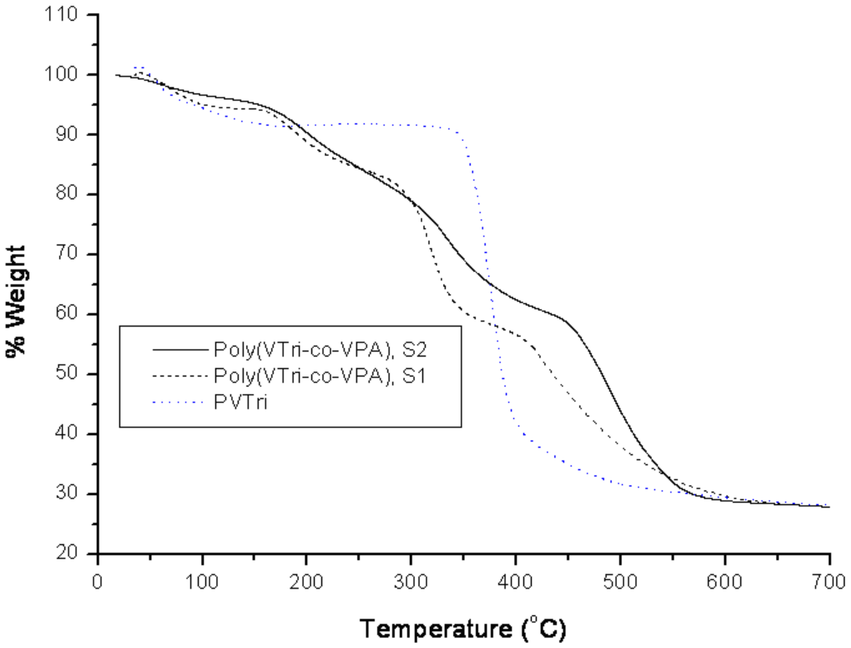

Figure S4: TGA thermograms of the homopolymer PVTri and Poly(VTri-*co*-VPA), S2 at a heating rate of 10 °C/min.

thermal stability under inert conditions. A gradual decay in weight of PVTri for temperatures up to 200 °C can be attributed to the loss of absorbed humidity. Above 350 °C a remarkable weight loss occurs due to thermal decomposition of triazole groups and the polymer main chain. Both copolymers poly(VTri-*co*-VPA) (**S1** and **S2**) illustrate a weight change up to approximately 150 °C which can be due to anhydride formation as well as evaporation of water from these hygroscopic materials. At higher temperatures (T>150 °C), further condensation and the decomposition of the copolymer main chain occur.

Differential scanning calorimetry (DSC) investigations were performed to determine the glass transition temperatures of the copolymer samples. Previous DSC results illustrated that there is no distinct glass transitions for the copolymers, poly(VPA-*co*-4-VIm) up to the onset of degradation near 200 °C.[8] The reason was attributed to ionic crosslinking that restricted the cooperative segmental motions of the polymer chains.

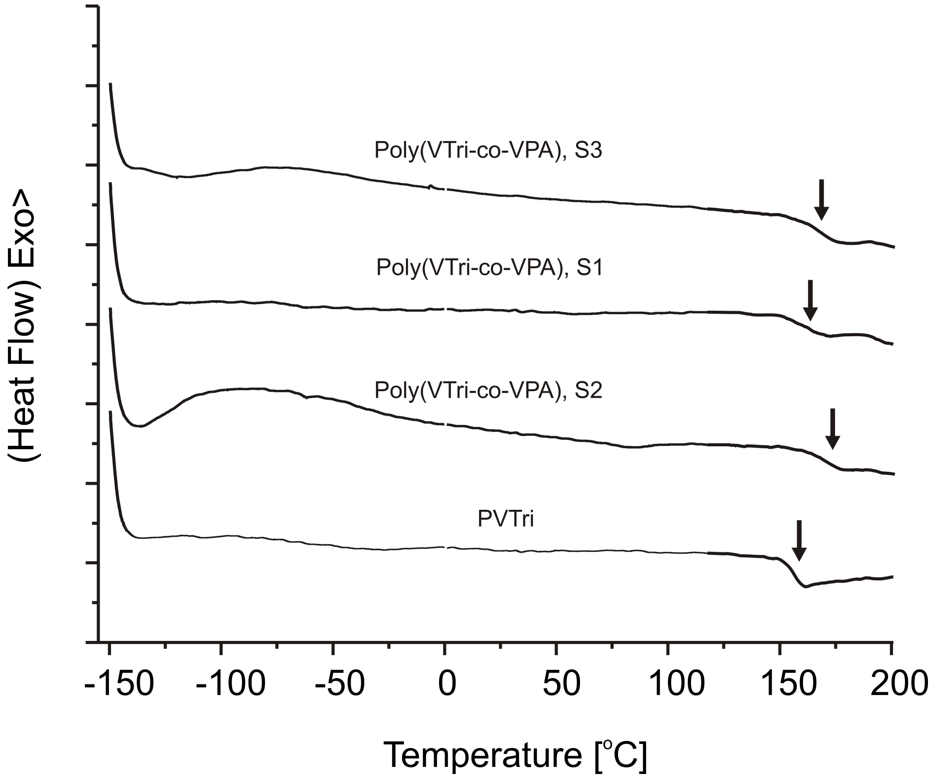

Figure S5: DSC curves of the copolymer samples recorded under inert atmosphere at a heating rate of 10 °C/min.

The DSC thermograms of the copolymer samples poly(VTri-*co*-VPA) (**S1**, **S2** and **S3**) are given in Figure S5. The PVTri homopolymer has a broad glass transitions at ~160 °C. The copolymer samples **S1**, **S2** and **S3** have definite glass transition at temperatures around 159 °C, 169 °C and 166 °C, respectively. These results demonstrate that the presence of ionic interactions does not prevent the cooperative relaxation of polymer chains. Moreover, the glass transitions of the copolymers do not vary systematically with the PVPA content and show only minor temperature shifts compared to the homopolymer PVTri. In pure PVPA, the glass transition temperature cannot be determined due to the condensation process at elevated temperatures.[9]

AC Conductivity Results:

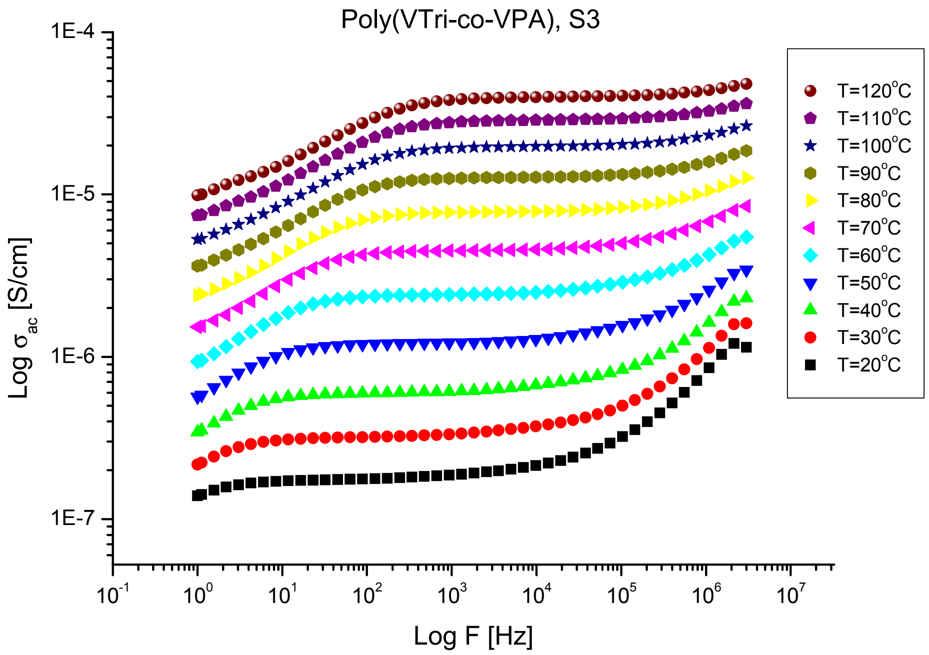

Figure S6: Log σ_{ac} vs. log F (Hz) of Poly(VTri-*co*-VPA), **S3** at various temperatures.

References of Supplementary Information:

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