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Mesomorphic Structure of Poly(styrene)-*block*-poly(4-vinylpyridine) with Oligo(ethylene oxide)sulfonic Acid Side Chains as a Model for Molecularly Reinforced Polymer Electrolyte

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ABSTRACT: We report self-organized polymer electrolytes based on poly(styrene)-*block*-poly(4-vinylpyridine) (PS-*block*-P4VP). Liquidlike ethylene oxide (EO) oligomers with sulfonic acid end groups are bonded to the P4VP block, leading to comb-shaped supramolecules with the PS-*block*-P4VP backbone. Lithium perchlorate ($LiClO_4$) has been added to the EO-rich domains. Small- and wide-angle X-ray scattering in combination with Fourier transformation infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), ac impedance, and dynamic mechanical spectroscopy (DMA) suggests alternating lamellae of reinforcing glassy PS domains and ionically conducting "nanochannels" consisting of poly(4-vinylpyridinium), oligomeric ethylene oxide sulfonates, and $LiClO_4$. The long period of the self-organization is ca. 300 Å. So far, the ionic conductivity levels remained relatively low, i.e., $10^{-7}-10^{-6}$ S/cm at room temperature and $10^{-5}-10^{-4}$ S/cm at 80 °C. However, as self-organization of polymeric supramolecules allows combining glassy reinforcing domains and well-plasticized domains consisting of oligomers with high segmental motions, there may exist possibilities to tune feasible combination of electrical and mechanical properties.

Introduction

Block copolymers form self-organized nanoscale structures based on competing interactions.[1,2] Their phase behavior is controlled by the architecture, the temperature, the chemical structure, and the volume fractions of the blocks, which in principle allow tailoring of several materials properties simultaneously by adjusting the microphases. "Block-copolymer-like" self-organization can also be based on supramolecules (for supramolecules, see ref 3) where the blocks are bonded by matching physical interactions, such as hydrogen bonds, coordination, or ionic interactions.[4−8] The comb architecture is of particular importance, as it for example offers a facile route to process intractable polymers.[9] In general, comb-shaped supramolecules can be regarded as "supramolecular block copolymers" as well as specific "polymer/solvent complexes". The latter aspect emphasizes that the local dynamics can be very different from that of the pure high molecular weight polymers and block copolymers due to incorporation of the oligomeric components. This aspect allows for example switching of protonic conductivity based on phase transitions.[6]

There is a vast literature on ionically conducting polymeric electrolytes.[10−13] The most widely studied "salt-in-polymer" system consists of poly(ethylene oxide) (PEO) where for example lithium perchlorate ($LiClO_4$) or lithium bis(trifluoromethylsulfonyl)imide has been dissolved. The aim is to achieve high mobility of the Li^+ cations but to avoid the additional mobility of the anions; so-called single-ion conductors have been pursued.[12,14,15] High molecular weight PEO is semicrystalline. The conduction takes place in the amorphous regions where the chain relaxations are not hindered. However, dissolution of salts tends to change the crystallinity and to increase the glass transition temperature, and therefore the conductivity of a high molecular weight PEO is a compromise between charge carrier mobility and salt concentration.

There has been a wealth of efforts to lower the glass transition temperature (T_g) and to suppress the crystallization:[11,12] Sufficiently short ethylene oxide oligomers do not crystallize and have reduced T_g due to a larger proportion of chain ends, but they have poor mechanical properties. Additional plasticizers, solvents, and ceramic additives have been mixed with PEO; PEO can be cross-linked, and the matrices can be swollen with solvents to improve conduction and flexibility.[12] Random copolymers[16,17] or block copolymers[18−22] can be used. "Internal" plasticization can be accomplished by branches or combs within PEO, where the enhanced side-chain relaxations improve the mobility of ions.[11,14,23−26] Finally, oligomeric ethylene oxide side chains can be covalently connected to several types of polymer backbones to form other types of comb copolymers.[11,26−31] Low-dimensional conductors due to self-organized or smectic lamellar structures have been constructed to suppress aggregation due

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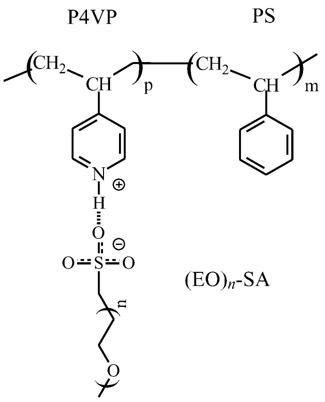
Scheme 1. Schematic Illustration of the Ionic Interaction between PS-*block*-P4VP and $(EO)_n$-SA; $LiClO_4$ Has Been Excluded



to the charges[32−40] which can lead to anisotropic conductivity.

The mechanical properties must also be considered: If the proportion of the chain ends is increased by reducing the molecular weight of the polyelectrolyte or if large amounts of side chains are incorporated in comb polymers, the mechanical properties may become poor. This can be overcome if the flexible side chains are incorporated within one block of a block copolymer, and the overall mechanical properties could be tailored by the other block.[18,19,39,40] Even a rigid backbone can be used.[41,42] Mesogenic moieties can also serve as reinforcements when they are connected with ethylene oxide repeat units.[37]

The present work has the following logic: (1) Ethylene oxide (EO) oligomers could form an interesting ion conducting medium, if they are sufficiently short and liquidlike. (2) The aim is to bond them within a diblock copolymers to form supramolecules, which, in turn, would form (possibly hierarchical) self-organization, in analogy to our previous protonic conductors.[6] (3) In contrast to the comb-shaped materials with the covalently bonded ethylene oxide side chains, we expected the physically bound side chains to have increased relaxations, which may improve the conductivity. In addition, the resulting low dimensionality of the conductors could lead to reduced ion aggregation. (4) One block was selected to consist of poly(styrene) (PS) in order to form lamellar glassy domains allowing molecular reinforcing. (5) $LiClO_4$ was soaked to the self-organized EO structures to promote ionic conduction.

On the basis of these arguments, we prepared samples where poly(styrene)-*block*-poly(4-vinylpyridine) (PS-*block*-P4VP) was complexed with (ethylene oxide)sulfonic acid, $(EO)_n$-SA. $LiClO_4$ was added to the EO phase leading to PS-*block*-P4VP($((EO)_n\text{-SA})_{1.0}(LiClO_4)_y$ complexes, where the $(EO)_n$-SA side chains are connected to the P4VP blocks using ionic interaction (Scheme 1). Complexes are characterized using Fourier transform infrared spectroscopy (FTIR), small- and wide-angle X-ray scattering (SAXS and WAXS), differential scanning calorimetry (DSC), dynamic mechanical spectroscopy (DMA), and ac impedance.

Experimental Section

Materials. Poly(styrene)-*block*-poly(4-vinylpyridine) (PS-*block*-P4VP) diblock copolymer was provided by Polymer Source Ltd. Molecular weights of the blocks were $M_{n,PS}$ = 40 000 g/mol and $M_{n,P4VP} = 5600$ g/mol, and the polydispersity was 1.09. Two oligo(ethylene oxide)sulfonic acids $CH_3-(OCH_2CH_2)_nCH_2-SO_3H$, i.e., $(EO)_n$-SA ($n = 8$, $M_w = 472$ g/mol and $n = 13$, $M_w = 672$ g/mol), were synthesized, using methods described elsewhere.[43,44] Essentially longer chains were expected to suffer from crystallization and therefore were abandoned. Lithium perchlorate $LiClO_4$ was provided by Fluka (98%). All materials were dried in a vacuum oven (ca. 10^{-2} mbar) at 25 °C for 3 days and at 60 °C for 3 h. The samples were prepared from tetrahydrofuran (THF) (Riedel-de Häen, 99.9%).

Sample Preparation. Samples were prepared using the two oligo(ethylene oxide)sulfonic acids with different chain lengths and samples with or without lithium perchlorate. PS-*block*-P4VP, $(EO)_n$-SA, and $LiClO_4$ were added into THF, and the solutions were stirred for 3 days. Mixtures were clear, and THF was evaporated at 25 °C and samples were dried in a vacuum oven (ca. 10^{-2} mbar) at 25 °C for 3 days and at 60 °C for 3 h. The complexes were denoted as PS-*block*-P4VP($((EO)_n\text{-SA})_{1.0}(LiClO_4)_y$, indicating that there is one $(EO)_n$-SA molecule vs one 4-vinylpyridine repeat unit and y $LiClO_4$ molecules (y = 0 or 1.0) vs one $(EO)_n$-SA side chain.

Fourier Transform Infrared Spectroscopy (FTIR). Protonation of P4VP nitrogens was investigated using Nicolet Magna 750 FTIR-spectrometer at room temperature. A minimum number of 128 scans were averaged at a resolution of 2 cm^{-1}. Samples were analyzed from films cast on potassium bromide crystals. The solvent was evaporated in a vacuum oven (ca. 10^{-2} mbar) at 25 °C for 3 days.

Small-Angle X-ray Scattering (SAXS). A small flake of the sample was placed between two pieces of copper. Measurements were performed using a sealed fine focus Cu X-ray tube in a point-focus mode.[5] The Cu Kα ($\lambda = 1.54$ Å) radiation was monochromatized with a Ni filter and a totally reflecting mirror (Huber small-angle chamber 701). Scattered radiation was detected by a one-dimensional proportional counter (MBraun OED-50M). The distance between the sample and the proportional counter was 1180 mm.

Wide-Angle X-ray Scattering (WAXS). WAXS experiments were performed using a Siemens $\theta-2\theta$ diffractometer in a symmetrical transmission mode with Cu Kα radiation, which was monochromatized with a quartz monochromator in the incident beam. The scattering intensities were detected using a scintillation counter with an angular range of 5°−40°, an angular step of 0.1°, and a measurement time of 90 s per point.

Differential Scanning Calorimetry (DSC). The transition temperatures and the crystallinity were investigated using a Mettler Toledo Star DSC821 differential scanning calorimeter under a nitrogen atmosphere. Samples were first cooled from the room temperature to −80 °C with a cooling rate of −10 °C/min, and DSC curves were scanned from −70 to 60 °C with a heating rate of 10 °C/min. High temperatures were avoided due to the risk of thermal decomposition of $LiClO_4$. The sample weight was typically 10 mg. The T_g was taken as a midpoint of the transition and the melting temperature (T_m) as the peak position in the DSC curve.

Dynamic Mechanical Spectrocopy (DMA). Dynamic mechanical properties were measured as a function of temperature using Perkin-Elmer dynamic mechanical analyzer (DMA7) in a three-point bending mode. The span between the supports was 5 mm, and the sample length, width, and height were 8, 3, and 1 mm, respectively. The samples were cooled from the room temperature to −100 °C using cooling rate less than −3 °C/min. The storage (E') and the loss modulus (E'') were measured under helium atmosphere from −90 to 120 °C using the heating rate 4 °C/min and frequency 1 Hz. The amplitude was selected to be constant (3 μm) during the measurement. A dynamic stress was between 500 and 800 kPa at −90 °C, depending on the sample and a static stress 10% higher than the dynamic stress. The transition temperature was recorded as a peak in the loss modulus curve.

Ac Impedance. The conductivities were studied using a HP 4192LF impedance analyzer at frequencies 10 Hz−10 MHz. The PS-*block*-P4VP($((EO)_n\text{-SA})_{1.0}(LiClO_4)_y$ films were cast from THF solution on a glass plate with gold electrodes and were dried in a vacuum oven (ca. 10^{-2} mbar) at 25 °C for 3

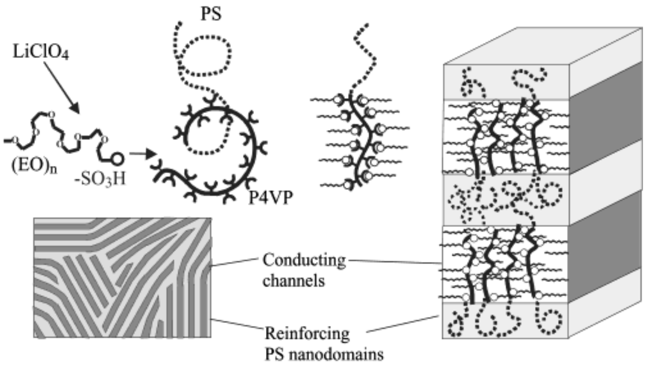


Figure 1. Schematic illustration of the immobilization of ethylene oxide oligomers to P4VP nitrogens of PS-*block*-P4VP block copolymer, based on the protonation of the sulfonic acid end groups. A lamellar structure with a long period of ca. 300 Å is formed. The glassy PS domains act as molecular reinforcements and the oligomeric EO molecules as an ionically conducting medium. Note that although the structure is at the local scale anisotropic and self-organized, they have not been aligned, and the reinforcement is isotropic on the macroscopic scale.

days and at 60 °C for 3 h and before measurement stored in dry atmosphere. In the measurement setup the samples were sealed between two glass plates to avoid absorption of humidity. The conductivity of the sample was determined on the basis of the intermediate frequency plateau extrapolated to zero frequency. The samples were first cooled from the room temperature to −50 °C, and the measurements were performed in the temperature range 0−80 °C using heating rate of 1 °C/min.

Results and Discussion

The aim was to bond the ethylene oxide oligomers within self-organized polymeric nanostructures, still allowing high segmental relaxations. Within the concept, the glassy PS domains of PS-*block*-P4VP would reinforce the structures and P4VP would bind the end-functionalized plasticizing oligomers for example by hydrogen bonding, coordination, or ionic interaction.[4−8] Our previous experience suggested that phenols are sufficiently acidic to allow strong hydrogen bonding to bind long alkyl tails (15−19 methylenes) to P4VP and to form comb-shaped supramolecules.[5,45] However, if the alkyl tail length exceeds ca. 23 methylene units, a macrophase separation takes place. Therefore, to ensure sufficiently strong interaction, ionic interaction due to proton transfer is used (see Figure 1). The side chains of the resulting comb-shaped poly(4-vinylpyridinium) oligo(ethylene oxide)sulfonates [P4VP((EO)$_n$-SA)$_{1.0}$] were expected to act as plasticizers, in analogy with P4VP quaternized with ethylene oxide oligomers.[29] In the present case, the P4VP chains have further been covalently connected to PS due to the diblock copolymer architecture. The molecular weights of the blocks were selected to lead to alternating P4VP((EO)$_n$-SA)$_{1.0}$ and glassy PS lamellae. Finally, since in P4VP quaternized with ethylene oxide oligomers with either bromide or chloride counterions the side chains are prone to crystallize if they contain at least ca. 14 EO repeat units,[29] we selected relatively short side chains, i.e., $n = 8$ and 13.

First we studied whether the ionic bonding between the P4VP nitrogens and (EO)$_n$-SA takes place. Figure 2 shows the FTIR spectra of LiClO$_4$, (EO)$_8$-SA, PS-*block*-P4VP, PS-*block*-P4VP((EO)$_8$-SA)$_{1.0}$, and PS-*block*-P4VP((EO)$_8$-SA)$_{1.0}$(LiClO$_4$)$_{1.0}$ in the region from 1425 to 1675 cm^{-1}. (EO)$_8$-SA is used as a typical example, but similar behavior is observed for (EO)$_{13}$-SA. A flat intensity maximum for LiClO$_4$ at 1629 cm^{-1} and for (EO)$_8$-SA at 1610 cm^{-1} makes the interpretation difficult. The spectra of PS-*block*-P4VP, PS-*block*-P4VP((EO)$_8$-SA)$_{1.0}$ and PS-*block*-P4VP((EO)$_8$-SA)$_{1.0}$(LiClO$_4$)$_{1.0}$ can be normalized using the sharp bands at 1451 and 1492 cm^{-1}, and the ratio of absorbance intensities can be qualitatively compared. The ring stretching bands of PS and P4VP are at 1600 and 1597 cm^{-1}, respectively, and for the block copolymer these bands overlap. When the nitrogens of P4VP are protonated using a strong acid, this band shifts to higher wavenumbers. For PS-*block*-P4VP((EO)$_8$-SA)$_{1.0}$(LiClO$_4$)$_y$, a new band is formed at 1637 cm^{-1}, and at the same time the relative intensity of bands at ca. 1600 cm^{-1} decreases. This indicates that the nitrogens of P4VP have been protonated, and ionic interaction between P4VP and (EO)$_8$-SA has been formed to achieve a comb-shaped supramolecule (see Figure 1). Protonation of P4VP might also be studied in the region around 1000 cm^{-1}, but there are several overlapping peaks of (EO)$_8$-SA and LiClO$_4$, making the interpretation even more difficult.

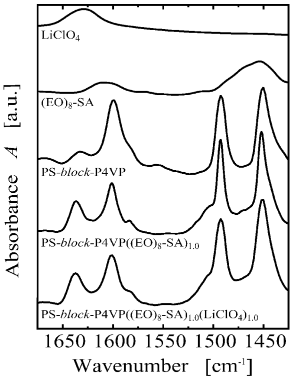


Figure 2. FTIR spectra of LiClO$_4$, (EO)$_8$-SA, PS-*block*-P4VP, PS-*block*-P4VP((EO)$_8$-SA)$_{1.0}$, and PS-*block*-P4VP((EO)$_8$-SA)$_{1.0}$-(LiClO$_4$)$_{1.0}$ at the region from 1425 to 1675 cm^{-1}. The overlapping ring stretching bands of PS and P4VP are at 1600 and 1597 cm^{-1}, respectively. When the nitrogens of P4VP are protonated using (EO)$_8$-SA, a shifted band is observed at 1637 cm^{-1} and the relative intensity of bands at ca. 1600 cm^{-1} decreases.

The structure formation and crystallinity of the solvent-free samples were investigated at room temperature. Figure 3a shows the SAXS intensity patterns as a function of the magnitude of the scattering vector $q = 0.01-0.10$ Å^{-1}. There were no clear SAXS peaks for (EO)$_8$-SA, (EO)$_{13}$-SA, and LiClO$_4$ in this region. PS-*block*-P4VP shows a broad peak at $q_1 = 0.030$ Å^{-1} and a faint shoulder at about 0.048 Å^{-1} ($\approx 1.6q_1$). As the weight fraction of P4VP in the block copolymer is $f_{\mathrm{P4VP}} = 0.12$, it is probable that this polymer forms a spherical structure with a long period of 210 Å. For PS-*block*-P4VP((EO)$_n$-SA)$_{1.0}$, equally spaced peaks were observed at $1q^*$, $2q^*$, $3q^*$ ..., indicating lamellar structures. The long periods were 300 and 270 Å for $n = 8$ and 13, respectively. Astonishingly, the long period is shorter for the longer side chains. The conformation of P4VP and the thickness of P4VP((EO)$_n$-SA)$_{1.0}$ lamellae probably do not depend considerably on the length of the side chains, because both of such side chains are relatively long and the P4VP block is fairly short. On the other hand, the cross section needed for one P4VP block at the interface between the PS- and P4VP((EO)$_n$-SA)$_{1.0}$ phases increases as a function of the side chain

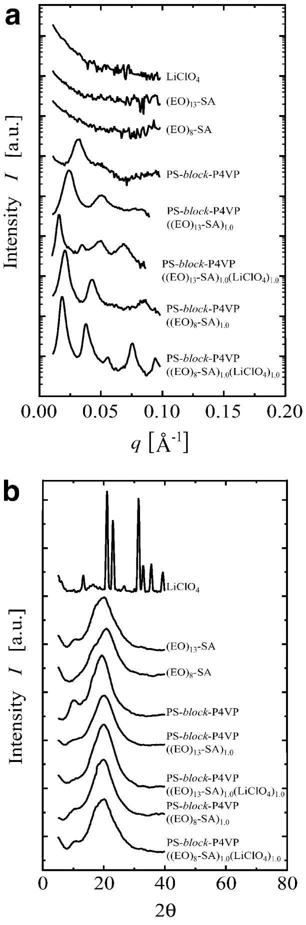


Figure 3. (a) SAXS and (b) WAXS intensity patterns of $LiClO_4$, $(EO)_{13}$-SA, $(EO)_8$-SA, PS-*block*-P4VP, and their complexes PS-*block*-P4VP($(EO)_n$-SA$)_{1.0}$ and PS-*block*-P4VP($(EO)_n$-SA$)_{1.0}$($LiClO_4$$)_{1.0}$ at room temperature. The curves indicate that complexes form amorphous lamellar structures.

length, probably decreasing the thickness of the PS lamellae and the long period. In the case of PS-*block*-P4VP($(EO)_n$-SA$)_{1.0}$($LiClO_4$$)_{1.0}$ the long periods were 330 and 370 Å for $n = 8$ and 13, respectively. Addition of salt increases the long period. The influence of the salt on the long period is difficult to explain, because the salt addition may also affect on the conformation of $(EO)_n$-SA. SAXS measurements were extended also to the region $q = 0.1-0.6$ Å^{-1}, but there were no sharp peaks observed; therefore, the data are not presented. Figure 3b shows WAXS intensity patterns. There are many sharp peaks for $LiClO_4$ indicating crystallinity. For all other samples, there are only flat maxima, and they form amorphous structures at room temperature, indicating that the polymers dissolve $LiClO_4$. The results also show that the EO oligomers do not crystallize at room temperature, which is desirable because the conductivity of PEO in amorphous regions is much higher than that in the crystalline regions.

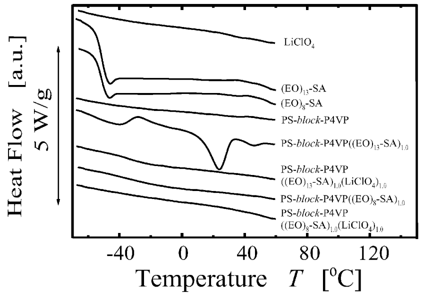


Figure 4. DSC traces of $LiClO_4$, $(EO)_{13}$-SA, $(EO)_8$-SA, PS-*block*-P4VP, and their complexes PS-*block*-P4VP($(EO)_n$-SA$)_{1.0}$ and PS-*block*-P4VP($(EO)_n$-SA$)_{1.0}$($LiClO_4$$)_{1.0}$. The glass transition of $(EO)_n$-SA is observed at −54 °C, and PS-*block*-P4VP-($(EO)_{13}$-SA$)_{1.0}$ can crystallize when the temperature is lowered.

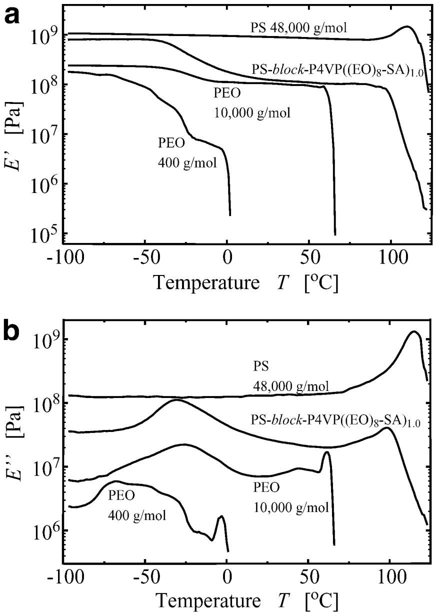


Figure 5. (a) The storage E' and (b) the loss moduli E'' as a function of temperature for PS homopolymer ($M_{n,PS} = 48\,000$ g/mol and $M_w/M_n = 1.03$), PS-*block*-P4VP($(EO)_8$−SA$)_{1.0}$, a medium molecular weight PEO ($M_{w,PEO} = 10\,000$ g/mol), and a oligomeric EO ($M_{w,PEO} = 400$ g/mol).

The glass transition temperatures T_g and melting temperatures T_m of the samples were measured in the temperature range from −70 to 60 °C using DSC (Figure 4). The temperatures were limited to moderate temperatures to avoid degradation of $LiClO_4$. Note that the melting temperatures of the functionalized ethylene oxide oligomers were expected to be much lower than that of the corresponding high molecular weight PEO (see also Figure 5a). T_g for $(EO)_8$-SA and $(EO)_{13}$-SA were observed around − 54 °C due to their short ethylene oxide chains, but no separate melting peak was seen. PS-*block*-P4VP($(EO)_{13}$−SA$)_{1.0}$ showed that in this case probably the oligo(ethylene oxide) side chains form crystalline structures at lower temperatures. T_m was observed at 23 °C, and cold crystallization was observed at lower temperatures during the heating. No clear T_g of this complex and T_g and T_m for other samples were observable. Note, however, that in PS-*block*-P4VP-($(EO)_{13}$-SA$)_{1.0}$($LiClO_4$$)_{1.0}$ there is a faint indication of glass transition at ca. −30 °C and that the crystallization has been suppressed due to addition of $LiClO_4$. In conclusion, the shorter oligo(ethylene oxide) chains are less prone to crystallize than the longer ones, as expected.

The storage E' and loss moduli E'' of PS-*block*-P4VP-($(EO)_8$-SA$)_{1.0}$ were next compared to those of a corresponding PS homopolymer ($M_{n,PS} = 48\,000$ g/mol, $M_w/M_n = 1.03$, Polymer Source Ltd.) and PEO homopolymers, one of which with a corresponding oligomeric length ($M_{w,PEO} = 400$ g/mol, Aldrich) and the other having a higher molecular weight ($M_{w,PEO} = 10\,000$ g/mol, Aldrich) (see Figure 5a,b). A sample without $LiClO_4$, i.e., PS-*block*-P4VP($(EO)_8$−SA$)_{1.0}$, is studied because it can be safely heated to temperatures exceeding 100 °C.

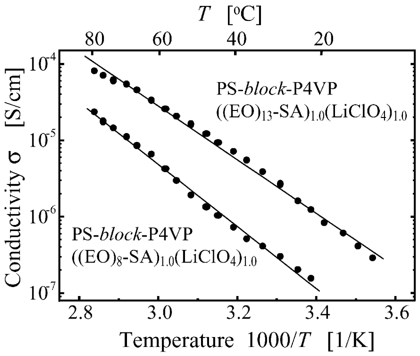


Figure 6. Dc conductivities of PS-*block*-P4VP$((EO)_8\text{-}SA)_{1.0}$-$(LiClO_4)_{1.0}$ and PS-*block*-P4VP$((EO)_{13}\text{-}SA)_{1.0}(LiClO_4)_{1.0}$ as a function of temperature.

Below the glass transition temperatures of both PS and PEO, all samples are hard, and E' of PS-*block*-P4VP-$((EO)_8\text{-}SA)_{1.0}$ is comparable to that of the PS homopolymer. When the temperature exceeds T_g of PEO, E' of PS-*block*-P4VP$((EO)_8\text{-}SA)_{1.0}$ decreases, reaching the value corresponding to the PEO homopolymer with $M_{w,PEO} = 10\,000$ g/mol. The pure PEO oligomer with $M_w = 400$ g/mol melts at −4 °C, forming a viscous fluid, leading to collapse of mechanical properties. Note that the molecular weight of the bonded oligo(ethylene oxide) side chains within PS-*block*-P4VP$((EO)_8\text{-}SA)_{1.0}$ is of the same order of magnitude as PEO oligomers, i.e., $M_w = 472$ g/mol. Homopolymeric PEO with $M_w = 10\,000$ g/mol melts at 62 °C, and above that E' decreases rapidly. When the temperature is further increased, E' of PS-*block*-P4VP$((EO)_8\text{-}SA)_{1.0}$ remains at a high level due to the nanoscale reinforcing glassy PS lamellae until T_g of PS (ca. 100 °C) is passed. In conclusion, the mechanical properties of PS-*block*-P4VP$((EO)_8\text{-}SA)_{1.0}$ supramolecules are controlled by the glassy PS domains.

Figure 6 shows the ionic conductivities of PS-*block*-P4VP$((EO)_8\text{-}SA)_{1.0}(LiClO_4)_{1.0}$ and PS-*block*-P4VP$((EO)_{13}\text{-}SA)_{1.0}(LiClO_4)_{1.0}$ as a function of temperature using ac impedance extrapolated to the zero frequency. The room temperature conductivities are 10^{-7} and 10^{-6} S/cm, respectively. The values are comparable to those of other self-organized PEO conductors in the bulk phase whereas substantially higher values have been obtained in Langmuir−Blodgett films, which potentially becomes from better alignment on the substrates.[36]

One can conclude that even if the observed conductivity levels as such are not particularly attractive, the properties in combination with dynamic mechanical properties are encouraging. High segmental motion has been considered to imply high conductivity in traditional salt-in-polymer systems.[12] In polymer-in-salt systems and superionic glasses the conductivity is decoupled from the segmental motions.[13] In particular, it has been emphasized that in the latter materials the shear modulus should have a separate low-temperature glass transition for the mobile ions in addition to the “main” structural glass transition, corresponding to relaxations at the time scale of the order of 100 s.[13] Interestingly, a apparently related behavior may be observed also in the present case based on another mechanism where the “structural” glass transition is at 100 °C due to the reinforcing glassy PS nanoscale lamellae, and the oligomeric PEO conduction medium has a much lower T_g close to −30 °C. Therefore, it seems that our concept may in principle be very attractive. The actual optimum compositions leading to high conductivity could be at a narrow composition window, as has been observed in PEO/novolac/$LiClO_4$ systems.[46] It may also be feasible to replace the ionic interaction between the ethylene oxide oligomer and P4VP by essentially uncharged hydrogen bonding which could make reduce the depth of Coulombic traps. The single ion system might also be achieved by replacing the present comb-shaped architecture with oligomeric $(EO)_n\text{-}SO_3Li$ bonded within the self-organized microphases of a block copolymer poly(vinylphenol)-*block*-poly(styrene) and tailoring n.

Conclusions

We have bonded ethylene oxide (EO) oligomers within self-organized polymer structures by binding them ionically to the pyridine groups of PS-*block*-P4VP using sulfonic acid end groups of the EO oligomers. $LiClO_4$ has been added presumably into the PEO parts, and the compositions are denoted as PS-*block*-P4VP$((EO)_n\text{-}SA)_{1.0}(LiClO_4)_{1.0}$. The molecular weights of the components have been selected to form lamellar structures consisting of alternating glassy PS and ionically conducting microphases. The long periods of complexes without salt were about 300 Å, and addition of the salt caused increased long period. PS-*block*-P4VP$((EO)_n\text{-}SA)_{1.0}(LiClO_4)_{1.0}$ is amorphous at 30 °C, and PS acts as molecular level reinforcement, improving the mechanical properties in comparison with the ethylene oxide oligomers. The conductivity at the room temperature was about 10^{-7} and 10^{-6} S/cm for $n = 8$ and $n = 13$, respectively. The present work shows that self-organization within block copolymers or supramolecules leads to another route of decoupling between the structural and conduction medium relaxations.

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