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Radical copolymerization of potassium 4-vinyl biphenylsulfonylimide and oligo(oxyethylene) methacrylates. Thermal behavior and single-ion conductivity of the copolymer electrolytes formed

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Summary

Radical copolymerization of potassium 4-vinyl biphenylsulfonylimide (K-4VPSI) and a series of oligo(oxyethylene) methacrylates $(EO)_nMA$ (n=3, 9 and 22) has been carried out in aqueous medium. Free radical copolymerization reactivity ratios were determined. They indicate a statistical copolymerization for n=9 and a tendency to alternation for n=22. When $n \geq 9$, significant single ion conductivity values are obtained at lower salt concentrations, where the mobility of the polyelectrolytes is highest. The K-4VPSI / $(EO)_9MA$ copolymers present a domain of salt content where a leveling of conductivity is observed, due to aggregation.

Introduction

Ion-conductive polymers, usually lithium salts dissolved in a solvating polymer matrix, find their application in solid state, high-energy, batteries. To avoid the decrease in conductivity under d.c. polarization due to migration of both cation and anion, single ion conductive systems have also been explored [1-12].

In our search for new performing polymer electrolytes two types of lithium salts have been investigated : perfluoroalkylsulfonates [13] and a homologous series of phenylsulfonylimides [14-16]. Single ion-conductors derived from lithium perfluoroalkylsulfonates $RFSO_3Li$ [17] tethered to a poly(oxyethylene) based network have already been prepared.

We describe here an other approach to single-ion conductors based on copolymers of a carrier source monomer, alkali 4-vinyl biphenylsulfonylimide, and oligo(oxyethylene) methacrylates, as ion solvating monomers. The present paper investigates the feasibility of such polymer electrolytes using the potassium salt of 4-vinyl biphenylsulfonylimide (K-4VPSI). The preparation of the copolymers was achieved by means of radical copolymerization in aqueous medium. Reactivity ratios of K-4VPSI and oligo(oxyethylene) methacrylates $(EO)_nMA$ were determined to have some insight into the homogeneity of the copolymers. Subsequently copolymers were prepared at various degrees of conversion. Their thermal properties and single-ion conductivity are reported.

Experimental

Materials

Oligo (oxyethylene) methacrylates $CH_2=C(CH_3)COO(CH_2CH_2O)_nCH_3$ with average values of n equal to 9 ([$(EO)_9MA$]) and 22 ([$(EO)_{22}MA$]) were acquired from Polysciences. $(EO)_3MA$ having a oligo(ethylene glycol monoethyl ether) substituent was purchased from Aldrich. Before polymerization the monomers were purified by elution of their ether solution over a prepacked column (Aldrich) containing hydroquinone type inhibitors removers.

K-4VPSI synthesis and characterization

Potassium 4-vinyl biphenyl sulfonylimide (K-4VSP), was synthesized according to a general procedure already described [14]. Potassium benzene sulfonamide was synthesized by reacting benzene sulfonamide (Aldrich) (50 g, 0.256 mol) with aqueous KOH 2N (120 ml, 0.256mol) and mixing for two hours. This solution is directly added to an ether solution of styrene sulfochloride (25.856 g, 0.128 mol) and the inhomogeneous solution is mixed vigorously for 6 hrs. The benzene sulfonamide formed precipitates out. After three crystallizations in water, at 50°C, K-4VSP is obtained at 55% yield.

$C_{14}H_{12}NO_4S_2K$ (361.47) : Calc. C 46.52, N 3.89, H 3.35, K 10.82 Found C 46.20, N 3.90, H 3.32, K 11.0. FAB spectrometry : $(M+H)^+=362$, $(M+K)^+=399.9$.

^1H NMR (DMSO-d_6) : 5.297, 5.352 (d, 1H, $H_2C=$) ; 5.839, 5.928 (d, 1H, $H_2C=$) ; 6.674, 6.727, 6.761, 6.816 (q, 1H, =CH-) ; 7.336, 7.368, 7.417, 7.458, 7.581, 7.622, 7.660 (m, 9H, ar)

^{13} C NMR (DMSO-d_6) : 146.38 ($C_{1'}$), 145.71 (C_1), 138.52 (C_4), 135.85 (C_α), 129.82($C_{4'}$), 127.69 ($C_{3'}$,$C_{5'}$), 126.40 ($C_{2'}$,$C_{6'}$), 126.00 (C_2,C_6), 125.41(C_3,C_5), 115.75 (C_β)

Radical homopolymerization and copolymerization of the two monomers

Poly[K-4VPSI] was obtained by polymerization at 0.193 $mol.l^{-1}$ monomer concentration in water and $3.87.10^{-3}$ $mol.l^{-1}$ concentration of $K_2S_2O_8$ initiator. Homopolymerization of oligo(oxyethylene) methacrylates $(EO)_nMA$ [19,20] was performed in aqueous solution, at 40°C, with monomer concentration below 5% by weight and $K_2S_2O_8$ initiator (2% mol versus monomer). Remaining monomer and initiator were separated from poly[oligo(oxyethylene)]methacrylates by ultrafiltration (1000-Mw-cutoff membrane) of the aqueous polymerization solution. Copolymerization was carried in water at 40°C with a concentration of 5% by weight of total monomers and $K_2S_2O_8$ initiator (2 mol% of total vinyl monomers). Oxygen was previously eliminated by 4 hours nitrogen flushing.

Methods of polymer electrolyte characterization and thermal analysis

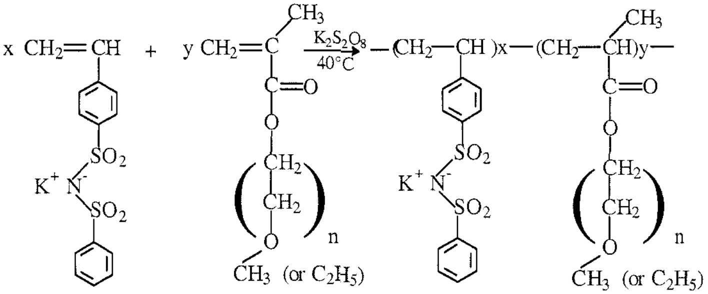
^1H NMR and ^{13}C-NMR spectra were recorded with a Brucker 200 spectrometer at room temperature. Glass transition and melting temperatures were obtained by differential scanning calorimetry on a Perkin-Elmer DSC 7 apparatus. Heating and cooling cycles at 20°C/min rate, between -130°C and +110 °C, were repeated until reproducible scans were obtained. Glass transition temperatures (T_g) were taken at the midpoint. The melting temperatures (T_m) were taken at the top of the transition.

Preparation of polymer electrolyte films and impedance analysis

Solutions of copolymers (500 mg) were poured onto a Teflon mold immediately after polymerization. The solvent was removed by room-temperature evaporation for 24 hours and then under progressively increasing vacuum for 48 hours, at 60°C. The polymer samples - about 0.2 mm thick - were sandwiched between stainless-steel blocking electrodes and placed in a glass oven attached to a vacuum pump.
Conductivity was measured with a Solartron 1260 impedance analyzer set (Schlumberger) at temperatures between 20°C and 80°C, over the frequency range of 1 Hz to 1 MHz.

Results and discussion

From the study of the series phenylsulfonylimide , bis(4-nitrophenyl)sulfonylimide and bis(2,4-dinitrophenyl)sulfonylimide salts [14-16] it ensues that the phenylsulfonylimides are interesting candidates to form single ion conductors, since their vinyl derivative K-4VPSI would allow radical copolymerization with oligo(oxyethylene)methacrylates, namely in aqueous medium.



Scheme 1. Radical copolymerization of K-4VSP and $(EO)_nMA$

Characterization of poly(K-4VPSI) and poly[(EO)$_n$MA] homopolymers

A poly(K-4VPSI) sample was studied in both dimethyl sulphoxide (DMSO) and water solution. Its viscosity is typical of a polyelectrolyte and obeys the Fuoss equation $\eta sp / c = A / (1+Bc^{1/2})$. However the viscosity is much higher in water due to a greater electrostatic repulsion of the macromolecular coils. Addition of homo-ionic KI salt gives a viscosity behavior that obeys the Huggins relation $\eta sp / c = [\eta] + k' [\eta]c$. Light scattering in presence of KI gives very close Mw values (around $2.25x10^5$) in both solvents. A slightly higher value ($2.89x10^5$) is observed in pure DMSO confirming a low dissociation of the polyelectrolyte, whereas the pure aqueous solution shows an angular dependence at high dilution, typical of true polyelectrolytes.
DSC study shows that poly[$(EO)_3$MA] and poly[$(EO)_9$MA] are both amorphous (T_g

equal to -52°C and -63°C, respectively), whereas poly[$(EO)_{22}$ MA] is semi-crystalline (two melting peaks at 41°C and 44°C). SEC allowed to determine a Mw of about 2.24×10^5 (Mn=0.74×10^5) for poly[$(EO)_3$ MA], but was inappropriate for polymers with longer ethylene oxide chains.

Free radical copolymerization reactivity ratios

The variation of the monomer concentration was determined by ^{1}H NMR with a modest accuracy and did not allow a very precise calculation of the free radical copolymerization reactivity ratios (table1). Indeed the goal was rather to compare those ratios and thus have some insight on the variation of the copolymer composition with time. K-4VPSI is more reactive than its co-monomers toward both growing radicals involved. The K-4VPSI - $(EO)_9$ MA system leads to a statistical copolymer, whereas K-4VPSI / $(EO)_{22}$MA shows a greater tendency to form an alternated copolymer. This might be due to a steric effect on the reactivity of the growing poly[$(EO)_n$MA] radical. Indeed in aqueous medium one has to consider the strong polyelectrolyte effect due to poly(K-VPSI) and the influence of $(EO)_n$MA micellisation on its homopolymerization, depending on the size of the side chain [19].

Table 1. Free radical copolymerization reactivity ratios in aqueous solution

Comonomers	Fineman-Ross method	Kelen-Tüdös method	$r_{K\text{-}4VPSI}\cdot r_{(EO)nMA}$
$(EO)_9$MA /	$r_{(EO)9MA} = 0.3$	$r_{(EO)9MA} = 0.3$	0.6 ± 0.05
K-4VPSI	$r_{K\text{-}4VPSI} = 2.0$	$r_{K\text{-}4VPSI} = 2.1$	
$(EO)_{22}$MA / K-4VPSI	$r_{(EO)22MA} = 0.06$	$r_{(EO)22MA} = 0.02$	0.03 ± 0.02
	$r_{K\text{-}4VPSI} = 0.78$	$r_{K\text{-}4VPSI} = 0.64$	

Copolymers obtained before complete overall conversion for $(EO)_{22}$MA / K-4VPSI system

To reduce somewhat the heterogeneity in composition of the copolymers a tentative was made to stop the $(EO)_{22}$MA / K-4VPSI copolymerization at an incomplete overall conversion. The medium was deactivated at room temperature by dilution, immediately followed by addition of an inhibitor. The K-4VPSI (monomer A) conversion, $\pi_{A,exp}$, was determined by UV analysis at 258 nm using absorption data shown in table 2.

Table 2. UV extinction coefficients of aqueous solutions of monomers and poly(K-4VPSI)

	λ_{max} (nm)	ε
K-4VPSI	258	18 664
MAPOE (n = 9,22)	206	4 039
poly(K-4VPSI)	193 222	24 730 12 702

Afterwards the solution was ultra-filtrated to eliminate the K-4VPSI monomer and the $(EO)_{22}MA$ macromonomer. The amount of copolymer obtained was determined gravimetrically. Elemental analysis of the copolymer was used to determine its molar-A (K-4VPSI) units content, written as $\langle F_A \rangle_{exp}$, to differentiate from F_A, the instantaneous content at a given conversion. Table 3 shows conversions and compositions obtained for three different initial monomer contents f_{A0}. It also compares $\langle F_A \rangle_{exp}$ with a value $\langle F_A \rangle^*$, calculated with the assumption that only the two monomers are eliminated during ultra-filtration.

Table 3. K-4VPSI / $(EO)_{22}MA$ copolymers characterization after ultra-filtration.

Copolymer	f_{Ao}	$\pi_{A,exp}$ (a)	$\pi_{w,exp}$ (b)	$\langle F_A \rangle_{exp}$ (c)	π^* (d)	$\langle F_A \rangle^*$ (e)
18 i	0.05	0.8	0.188	0.19	0.21	0.19
16 i	0.1	0.6	0.12	0.23	0.15	0.40
17 i	0.2	0.7	0.26	0.35	0.32	0.44

(a) conversion of monomer A before ultra-filtration
(b) yield by weight of the copolymer obtained after ultra-filtration
(c) molar-A content of copolymer after ultra-filtration
(d,e) global molar yield, π^*, and molar-A content, $\langle F_A \rangle^*$, both calculated from $\pi_{A,exp}$ and assuming that $\pi_{w,exp}$ represents the total amount of copolymer formed :
molar yield of B : $\pi_B^* = [\pi_{w,exp}(f_{Ao}.M_{wA} + f_{Bo}.M_{wB}) - f_{Ao}.\pi_{A,exp}.M_{wA}] / f_{Bo}.M_{wB}$, where M_{wA} and M_{wB} represent the molar mass of A and B units, respectively
global molar yield : $\pi^* = f_{Ao}.\pi_{A,exp} + f_{Bo}.\pi_B^*$
Calculated molar-A content of the copolymer : $\langle F_A \rangle^* = f_{Ao}.\ \pi_{A,exp} / \pi^*$

The calculated value $\langle F_A \rangle^*$ agrees with $\langle F_A \rangle_{exp}$ only for copolymer 18i, with lowest K-4VPSI content. It is assumed that ultra-filtration also eliminates oligomers, rich in K-4VPSI units.

In case of copolymer 18i, where no loss of polymer is observed during ultra-filtration, an indication of heterogeneity was obtained by means of equation I [20].

Equation I : $\pi = 1-[M]/[M_0] = 1- (f_A/f_{Ao})^{\alpha} (f_B/f_{B0})^{\beta} (f_{A0}-\delta /f_A-\delta)^{\gamma}$

where $\alpha = r_B/(1-r_B)$; $\beta = r_A/(1-r_A)$; $\gamma = 1-r_A r_B/(1-r_A)(1-r_B)$; $\delta = 1-r_B/2-r_A-r_B$

This equation relies f_A to the overall molar conversion π of the monomers, knowing the free radical copolymerization reactivity ratios, and allows the determination of the instantaneous (F_A) and average ($\langle F_A \rangle$) molar A- content of the copolymer, as function of π (figure 1).

Thus a value of 0.21 can be calculated for $\langle F_A \rangle$ at the overall molar conversion π^* of copolymer 18i. This value is very close to both the previously calculated $\langle F_A \rangle^*$ and the experimental one, $\langle F_A \rangle_{exp}$. It means a satisfactory accuracy in the determination of r_A and r_B. The range of variation of the instantaneous value of F_A (0.34 to 0.09) is indicative of the heterogeneity of the copolymer.

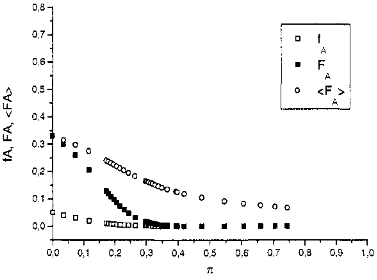


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Figure 1. Dependence of f_A, F_A and $<F_A>$ as function of overall molar conversion π, for $f_{A0} = 0.05$ (copolymer 18i), calculated from equation I for the K-4VPSI / $(EO)_{22}MA$ radical copolymerization.

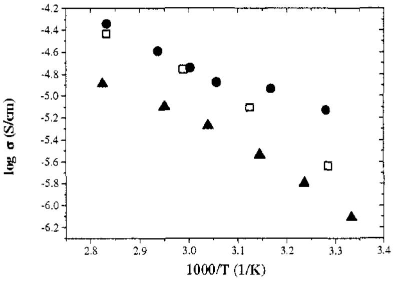

Figure 2. Arrhenius conductivity plots of K-4VPSI / $(EO)_{22}MA$ copolymers containing 0.19 (▲), 0.23 (□) and 0.35 (●) K-4VPSI molar unit fractions (copolymers 18i, 16i and 17i, respectively).

All three samples are semi-crystalline, but no regular variation of melting temperature T_m (24°C to 39°C) and melting enthalpy ΔH_m (29 to 77 J/g) with the concentration of salt is observed.

Figure 2 shows the Arrhenius plots of conductivity of the three polymer electrolytes. In the domain 40°C to 80°C, where they are totally amorphous, the conductivity σ increases with the salt content. The Tg of a true amorphous system is only measurable for copolymer 17i, with highest salt content, so that the influence of mobility could not be established. The conductivity values of copolymer 17i (4.3×10^{-5} and 8×10^{-6} S/cm, respectively at 80°C and 25°C) are comparable to other single Li^+ cation conducting systems [1,4,12].

Copolymers obtained at complete overall conversion

Due to the difficulty to obtain copolymers at controlled and limited conversion, a series of copolymers was prepared using different initial monomer compositions and running copolymerization up to complete monomer conversion. After 24 hours the solutions were still clear, but after ultra-filtration and drying a low fraction of the materials turned insoluble [18], though able to swell in solvents. Thus only solid state techniques were used for characterization. Compositions of the copolymers (table 4) differ from initial monomer compositions due to some oligomer elimination during ultra-filtration.

DSC data indicate that copolymers containing $(EO)_3MA$ units are amorphous and exhibit Tg values which vary linearly with molar salt concentration. This behavior is due to physical crosslinks by means of K^+ solvation by EO units [21].

Copolymers with $(EO)_9MA$ units are amorphous too, but present a phase segregation in the range of 17 to 31 molar percent of salt units, where two glass transition temperatures are observed. The lowest Tg's are close to the Tg value of homopoly[$(EO)_9MA$] (-62°C) and correspond to a domain with no or only few salt units. The second glass transition spreads over a very large domain of temperature and the Tg values rise with the salt content of the sample. It is to be related to a polymer-salt complex. Plotting 1/Tg versus O/K for the amorphous copolymers of the three series (figure 3) gives a rather regular variation from pure poly(K-4VPSI) to

Table 4. Composition and thermal properties of copolymers obtained at complete overall conversion, after ultra-filtration.

Co-polymer	$f_{A0}x10^2$	$<F_A>x10^2$	Tg_1 (°C)	$\Delta Cp_1x\ 10^2$ (J/g.°C)	Tg_2 (°C)	$\Delta Cp_2x\ 10^2$ (J/g.°C)	Tm (°C)	ΔH (J/g)
1 (n=3)	50	41	+78	4				
2 (n=3)	20	33	+59	24				
3 (n=3)	13	11	-40	66				
4 (n=3)	7	6.3	-46.3	60				
5 (n=9)	47	42	+14.9	50				
6 (n=9)	37.5	31	-8.3	25	-61.8	4		
7 (n=9)	31	28.7	-13.9	25	-64.1	13		
9 (n=9)	18	17	-48.1	76	-60.8	24		
10 (n=9)	15	16.1	-54	74				
11 (n=9)	10	11.4	-51	81				
12 (n=22)	68	63	+9.2	50				
13 (n=22)	52	54	-19.9	50			39.9	5
14 (n=22)	42	37.4	-38.8	48			41.1	37
15 (n=22)	35.4	32.5	-52.9	23			34	39
16 (n=22)	24	20.2	-54.9	23			38.7	68

copolymers of about 10% K-4VPSI units content, despite the heterogeneity in composition of the different samples. This indicates the dependence of the number of physical crosslinks on the oxygen atom over potassium cation ratio.

The series with $(EO)_{22}MA$ units is semi-crystalline, except the sample with highest salt content. The crystalline phase exhibits a melting temperature close to the value of pure homopoly[$(EO)_{22}MA$] (Tm=40°C), but its importance decreases when the overall salt content in the sample increases.

Conductivity values for the copolymers 1 - 4 (n=3) are very low, as an evidence that three ethylene oxide units are not enough to solvate properly the potassium cation [22,23].

Figure 4 shows the conductivity Arrhenius plots of copolymers 5 to 11 (n=9). The highest values of σ ($2.6x10^{-5}$ S/cm at 80°C for copolymer 11) are obtained for the lowest salt contents. Plotting log σ versus 1/(T-Tg) (figure 5) allows comparison at same mobility : the general trend observed is that conductivity increases with the salt content, though an inversion is observed for the lowest concentration. This suggests that the number of charge carriers increases with the salt content. However, the variation of log σ versus molar salt percentage at different reduced temperatures (figure 6) indicates an important increase of conductivity between 16% and 20%, followed by a plateau. This plateau defines a domain of mobility where the amount of dissociated species remains practically constant when the salt content rises. A possible explanation is the presence of aggregates as suggested by a glass transition that spreads over a large temperature scale. Such aggregates were already observed for some ionomers [24].

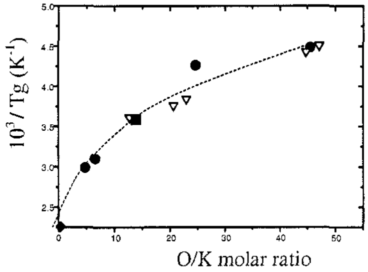

Figure 3. 1/Tg versus O/K molar ratio for amorphous K-4VPSI / $(EO)_nMA$ copolymers with n equal to 3 (●), 9 (∇), 22 (■) and homopoly(K-4VPSI) (♦).

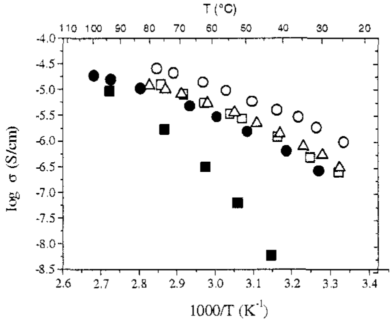

Figure 4. Arrhenius conductivity plots of copolymers containing $(EO)_9MA$ units at 42% (■), 31% (●), 17% (□), 16% (Δ) and 11% (○) molar percentages of salt.

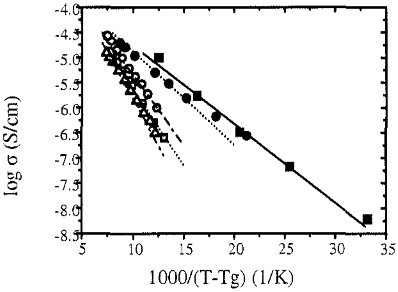

Figure 5. Conductivities versus reduced temperature of copolymers containing $(EO)_9MA$ units at 42% (■), 31% (●), 17% (□), 16% (Δ) and 11% (○) molar percentages of salt units.

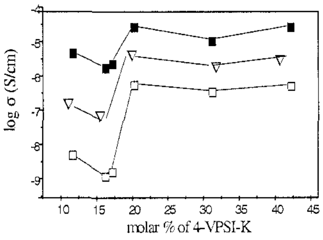

Figure 6. Conductivity of copolymers containing $(EO)_9MA$ units versus molar percentage of salt at 3 different reduced temperatures T-Tg : 100 K (■), 66.6 K (∇) and 55 K (□).

In case of copolymers 12-16 (n=22) the highest values of σ are again obtained for the lowest salt contents in the temperature domain were the systems are entirely amorphous. The influence of mobility could not be checked since quenching did not yield entirely amorphous systems. Nevertheless a limited comparison at close compositions and same temperature (80°C) is possible between the relatively homogenous copolymer 17i ($<F_A>_{exp}$ = 0.35, σ = 4.3×10^{-5} S/cm) and the heterogeneous copolymers 14 ($<F_A>_{exp}$ = 0.37, σ = 1.4×10^{-5} S/cm) and 15 ($<F_A>_{exp}$ = 0.32, σ = 1.3×10^{-5} S/cm). Clearly the former exhibits better conductivity.

The more even distribution of salt units along the chain in the more homogenous copolymer possibly favors the average solvation of K^+ by the oxyethylene units and thus increases the dissociation of the salt.

For the domain of concentration investigated the best conductivity values of potassium biphenylsulfonylimide based single ion conductors (4 to 5.10^{-5} S/cm at 80°C) compare with those obtained for potassium [12] and lithium [12, 25] perfluorosulfonates.

Conclusion

Homopolymers of potassium 4-vinyl-biphenylsulfonylimide (K-4VPSI) show polyelectrolyte nature when dissolved in water or DMSO solvent. The K-4VPSI monomer was able to copolymerize with oligo(oxyethylene) methacrylates $(EO)_nMA$. Free radical reactivity ratios of K-4VPSI / $(EO)_{22}MA$ and K-4VPSI / $(EO)_9MA$ aqueous copolymerizations indicate a higher reactivity of the K-4VPSI monomer toward the two growing radicals. For both the amorphous K-4VPSI / $(EO)_9MA$ and the semi - crystalline K-4VPSI / $(EO)_{22}MA$ polymer electrolytes, the highest single ion conductivities are observed for the lower salt contents. In the case of K-4VPSI / $(EO)_9MA$ this behavior could be related to a higher mobility, whereas an increase of the salt concentration levels the conductivity values.

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