Dielectric behavior of solid polymer electrolyte films formed by PEO-containing double hydrophilic block copolymers

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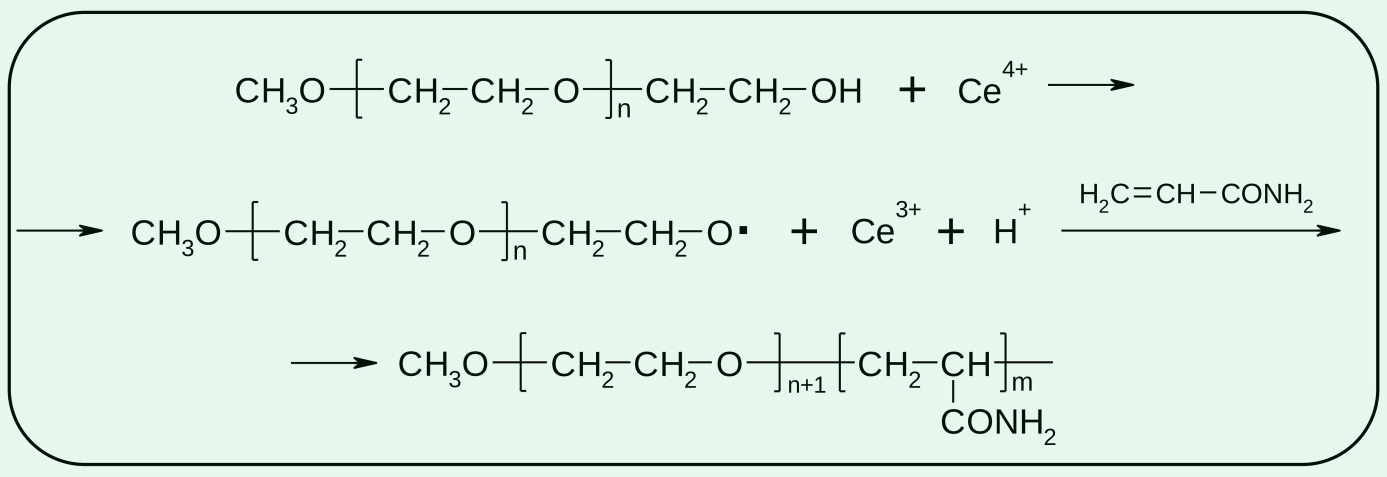
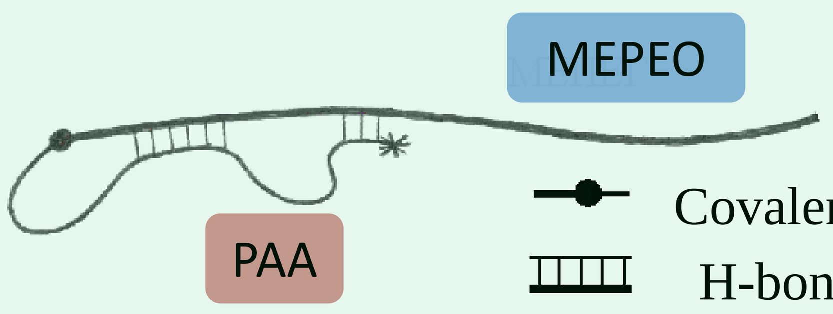
A solid polymer electrolytes (SPEs) with high ionic conductivity at room temperature has been an importance subject due to their interest in the all solid-state electrochemical devices development. Nowadays, the mainstream polymer matrix of the SPEs remains poly(ethylene oxide) (PEO). However, the high crystallinity of PEO leads to low ion conductivity and inferior Li^+ transference numbers (0.2–0.3) at room temperature, which affects the high rate capability of Li-batteries (LBs). We consider that the application of the PEO-contaning intramolecular polycomplexes (IntraPC) as polymeric matrices is eccentially more perspective since they allow to reduce PEO crystallization and demonstrate higher stability in many competitive processes, wich accompany the formation of multicomponent polymer electrolytes. In the present work we studied the ionic conductivity of graft copolymer comprising polyvinyl alcohol/polyacrilamide (PVA-*g*-PAAm), diblock- (DBC) and triblock (TBC) copolymers comprising chemically complementary poly(ethylene oxide)/polyacrylamide which form IntraPCs. We also examined DBCs and TBCs partially hydrolyzed derivatives (DBC_{hydr} and TBC_{hydr}) as possible ion-conducting membranes. Measurement of dielectric characteristics of the studied systems was performed in the frequency range 10^2-10^5 Hz using a dielectric spectroscope developed on the basis of the AC bridge P5083 and a three-electrode cell.

Synthetic methods for producing conductive polymers which form IntraPCs

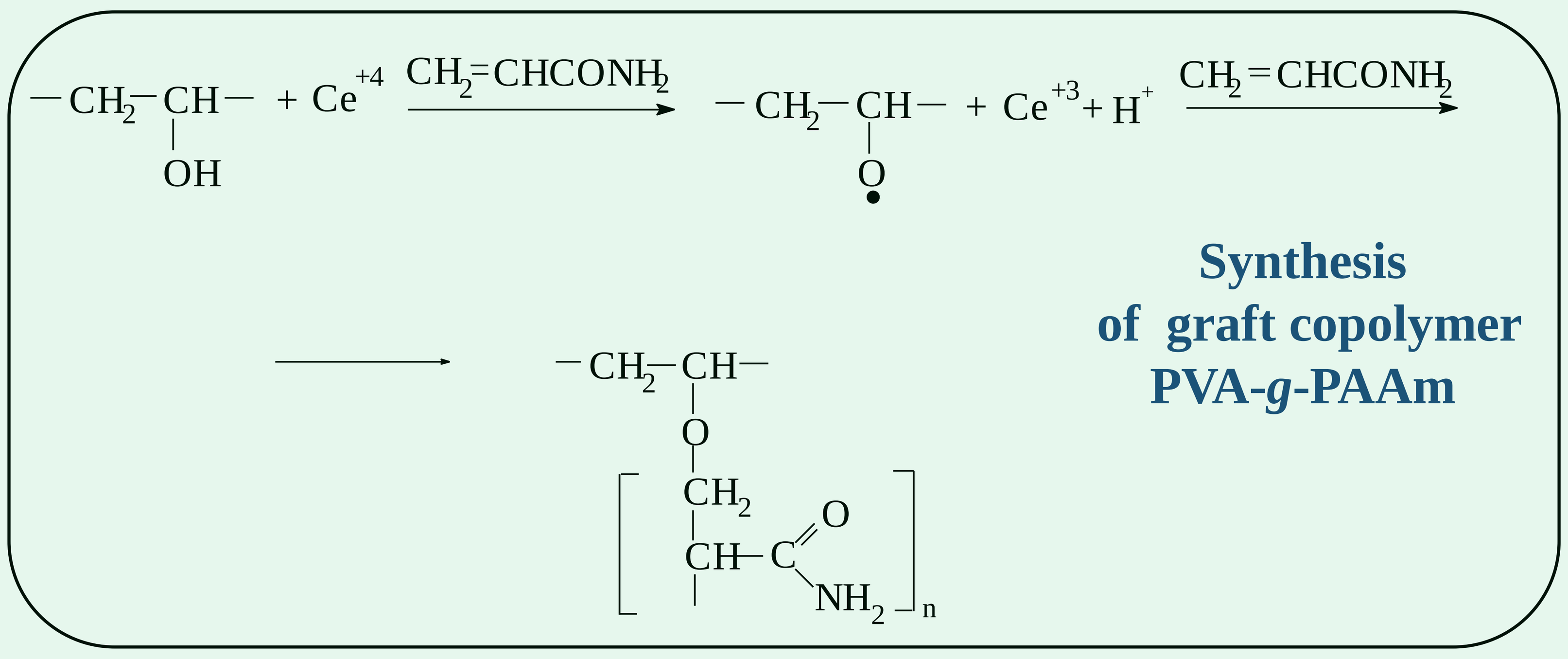


Synthesis of DBCs by the radical block copolymerisation of acrylamide and methyl ether of poly(ethylene glycol). To obtaine TBCs the poly(ethylene glycol) with Mn $35\cdot10^4$ kDa (TBC1) and $6\cdot10^4$ kDa (TBC2) were used.

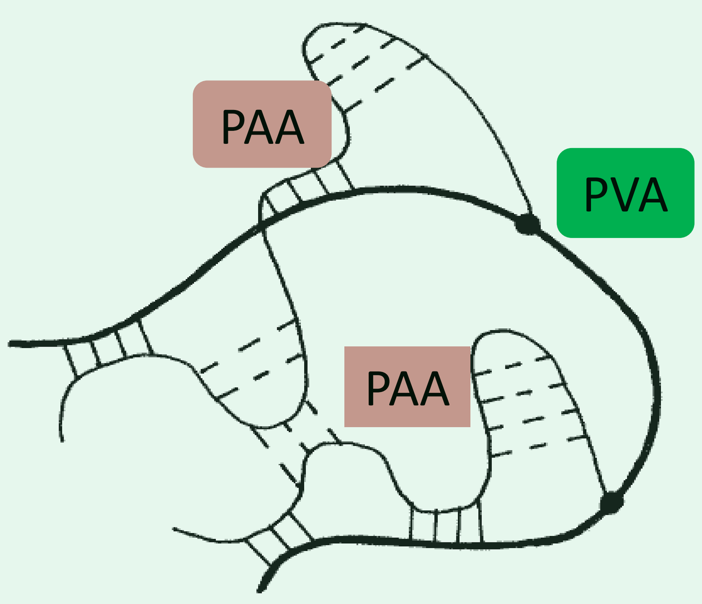


Covalent bonds between blocks
H-bonds between blocks
Active center of the growing PAAm chains

IntraPC formation in DBC

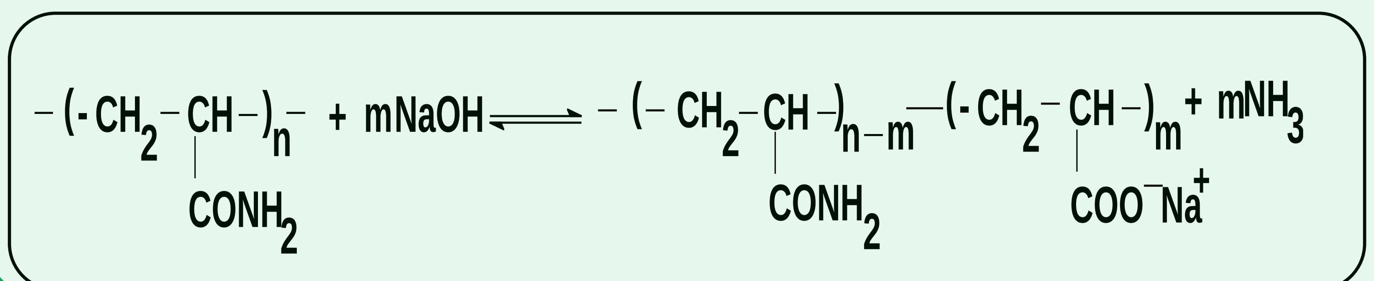


Synthesis of graft copolymer PVA-*g*-PAAm



Covalent bonds between PAAm chains
H-bonds between main and grafted chains
Grafts

IntraPC formation in PVA-g-PAAm



Introduction of -COOH-groups into DBCs /TBCs chains

Conclusion.

The obtained results allow to consider grafted and block copolymers with interacting blocks as promising matrices of electrolyte membranes and open ways for their application in Li-batteries, solar batteries and fuel cells. They also demonstrate the possibility of using biocompatible water-soluble solid polymer electrolytes in electrochemical devices and the implementation of their development at low cost and with high safety for the environment.

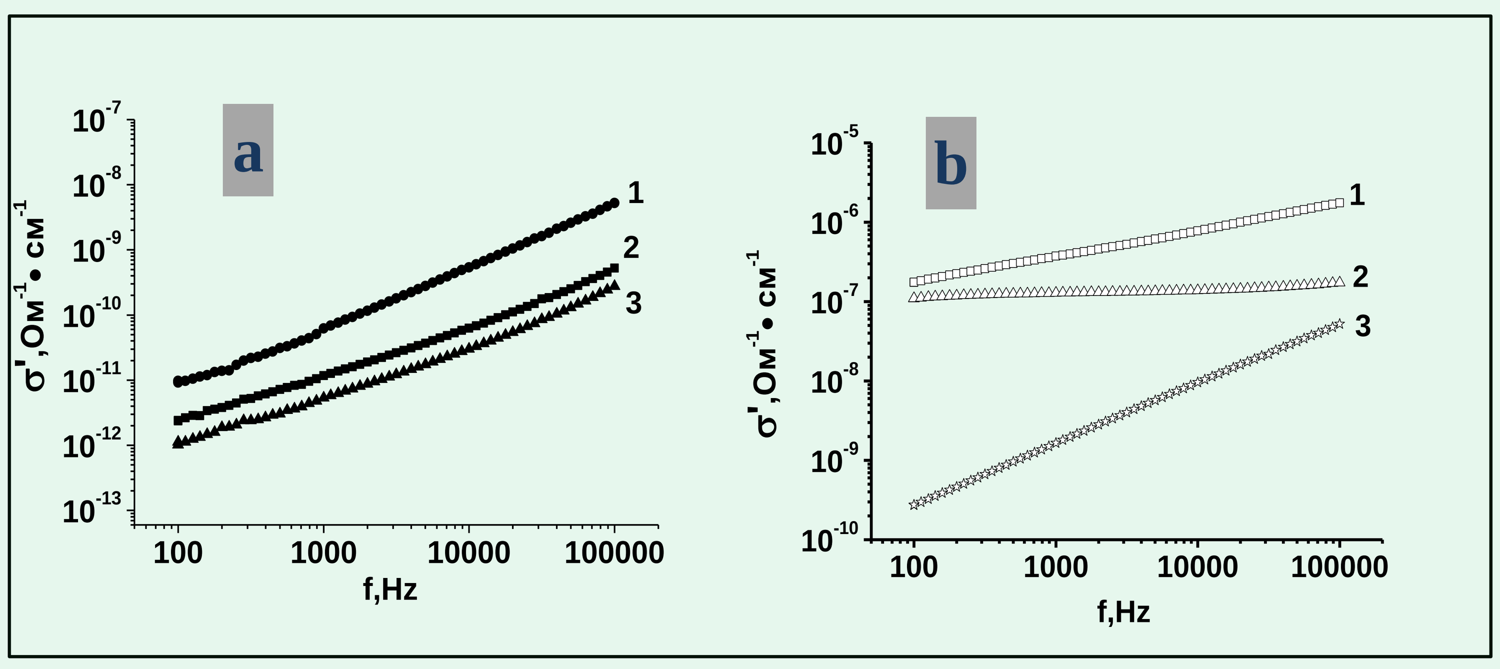
Conductivity of PEM based on double hydrophilic block copolymers which form IntraPCs

Table 1 - Conductive characteristics of DBCs, TBCs and PVA-*g*-PAAm membranes at a frequency 1 kHz

Copolymer	ε´	σ´, $S\cdot sm^{-1}$
DBC	5.37	$1.7\cdot10^{-10}$
DBC_{hydr}	16.2	$2.6\cdot10^{-9}$
PVA-*g*-PAAm	45.6	$8.8\cdot10^{-8}$
TBC1	5.7	$3.2\cdot10^{-9}$
TBC2	4.2	$6.2\cdot10^{-11}$
TBC_{hydr}	14.9	$1.7\cdot10^{-9}$

Table 2 - Conductive characteristics of DBCs, TBCs and PVA-*g*-PAAm membranes, dopted with $LiPF_6$, at a freguency 1 kHz

Copolymer	[PEO(PVA)]/[$LiPF_6$] base-mol·mol^{-1}	σ´, $S\cdot sm^{-1}$
DBC+$LiPF_6$	0.09	$1.7\cdot10^{-5}$
DBC_{hydr}+$LiPF_6$	0.09	$5.8\cdot10^{-7}$
PVA-*g*-PAAm+$LiPF_6$	0.09	$4.6\cdot10^{-10}$
TBC1+$LiPF_6$	0.09	$5.3\cdot10^{-8}$
TBC2+$LiPF_6$	0.15	$1.7\cdot10^{-10}$
TBC_{hydr}+$LiPF_6$	0.09	$1.3\cdot10^{-7}$



Dependences of the conductivity vs frequency for SPE membranes based on TBC1 (**a**) and TBC_{hydr} (**b**): without dopant –*3*(**a**), *3*(**b**); dopted with $LiPF_6$ at molar ratio [PEO]/[$LiPF_6$]=0.15 –*2*(**a**) and *2*(**b**); dopted with $LiPF_6$ at molar ratio [PEO]/[$LiPF_6$]= 0.06 –*3*(**a**) and *3*(**b**). T=25 °C.