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Synthesis, characterization and properties of microphase separated mixed (ionic and electronic) conducting or MIEC block copolymers are reported. Poly[ω -methoxyocta-(oxyethylene)methacrylate-block-4-vinylpyridine], abbreviated as P[MG8-4VP], and poly[3-methylthiophene-block- ω -methoxyocta(oxyethylene)methacrylate], abbreviated as P[3MT-MG8], have been synthesized. Both block copolymer series may be appropriately doped to generate separate electronic and ionic conducting microdomains in the overall solid matrix. Also, highly ionic conductive solid polymer electrolytes have been prepared by blending poly(ethylene oxide), poly(2- or 4-vinylpyridine) and LiClO₄. All blends were prepared by the solution blending process. Optimum blend compositions have been determined such that dimensionally stable elastomeric materials with ionic conductivities around $1.0 \times 10^{-5} \text{ S cm}^{-1}$ at 25°C are obtained.

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RESEARCH GOALS

The overall goal of the research project under research agreement No. DAAL03-89-G-0087 with the U.S. Army Research Office was to synthesize and characterize a new class of electroactive polymers. These polymers are block copolymers in which two incompatible electroactive blocks, an electronic conductive block and an ionic conductive block, are covalently connected. The polymers should form a microphase separated system and may be appropriately doped such that electronic conduction and ionic conduction are limited to separate phases. Figure 1, pictorially represents an idealized microphase separation in such systems. Here, cylindrical electronic conducting phases are immersed in an ionic conducting matrix. In essence developing a novel microphase separated mixed (electronic and ionic) conducting solid matrix. Such a system may be appropriately abbreviated as MIEC block copolymers.

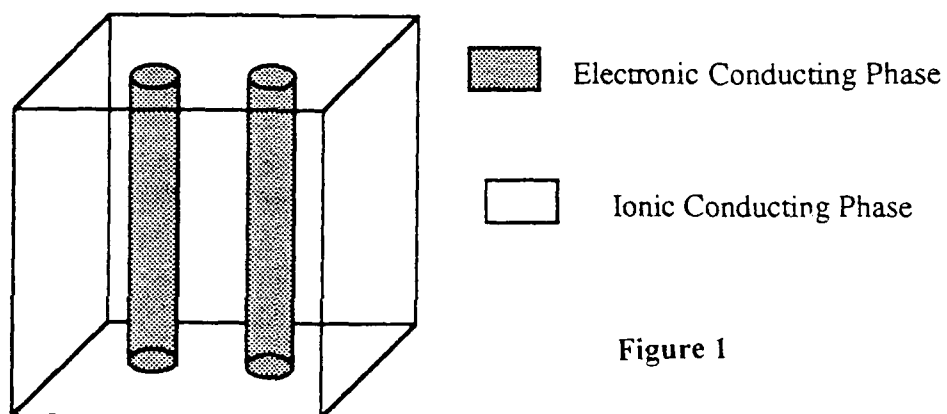


Figure 1

The proposed development of such MIEC block copolymers could conceivably have a major impact on micro/nanoelectronic technology. Possible applications include elastomeric electrodes in solid state cells, active component in sensors, photoelectrochemical displays and ultrathin membranes between an electrode and a polymer electrolytes in a solid state cell. Solvent free sensors require a microelectrode/thin ionic media combination. In the solid state morphology depicted in Figure 1, the electron conducting microdomain will act as a micro/nanoelectrode in excellent contact with the surrounding ionic media. Therefore, any small changes in the chemical potential of the ionic media should be readily detectable i.e. very fast response times with high sensitivities.

We have accomplished our goal by synthesizing, characterizing and determining the electronic properties of two groups of MIEC block copolymers. Additionally, we have developed a methodology of preparing highly ionic conductive blends using high molecular weight commercial polymers. Research accomplishments may be divided into two parts as follows:

A) Microphase separated mixed(ionic and electronic) conductive block copolymers or MIEC block copolymers.

B) Highly Conductive Solid Polymer Electrolytes prepared by Blending high molecular weight commercial polymers.

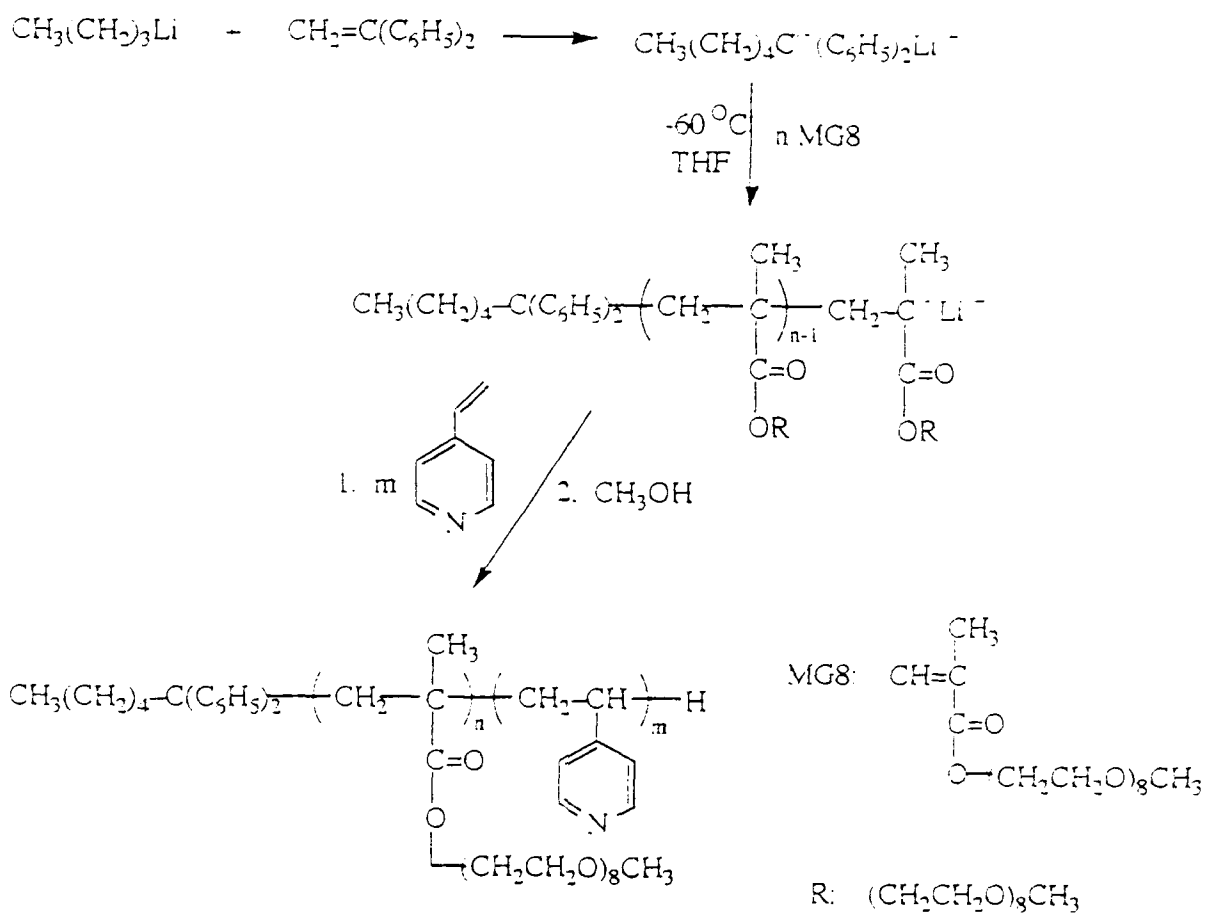
SUMMARY OF RESEARCH ACCOMPLISHMENTS

A) Microphase separated mixed(ionic and electronic) conductive block copolymers or MIEC block copolymers.

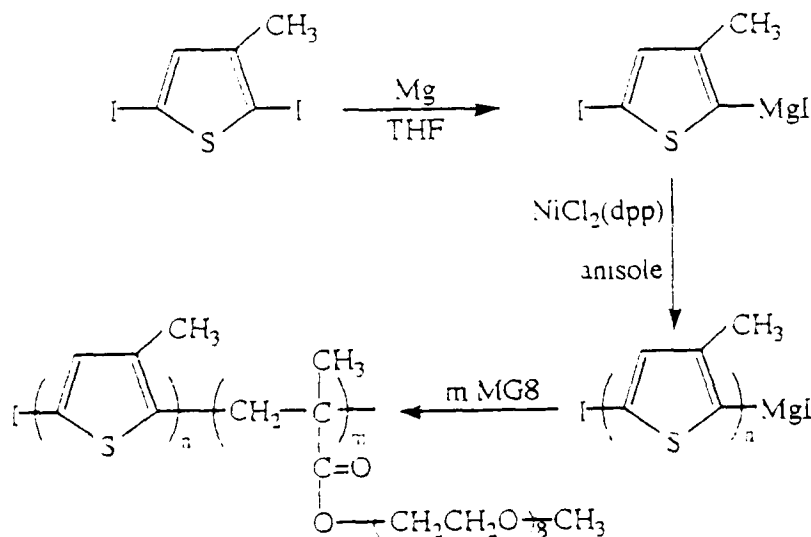
Two series of MIEC block copolymers have been prepared and characterized. Poly[ω -methoxyocta(oxyethylene)methacrylate-block-4-vinylpyridine], abbreviated as P[MG8-4VP], is outlined in Scheme 1. Experimental details are available in reference 1. Scheme 2 outlines the synthesis of poly[3-methylthiophene-block- ω -methoxyocta(oxyethylene)methacrylate], abbreviated as P[3MT-MG8]. The details of the synthesis have been submitted for publication (Reference 2) and a description of the process is given here. All polymerization reactions were carried out under dry nitrogen. Magnesium turnings were placed in a 100 ml three necked flask equipped with a reflux condenser, a pressure equalizing addition flask and a rubber septum. The magnesium turnings were dried by heating overnight under a N_2 stream. The flask was cooled to room temperature, 50 ml THF was introduced through the septum and 2,5-diiodo-3-methylthiophene (equimolar to Mg turnings) was added dropwise. The resulting mixture was refluxed for five hours. After most of the THF was removed under vacuum, the residue was dissolved in 30 ml. of anisole and a suspension of $NiCl_2(dpp)_2$, 4.0×10^{-3} moles per mole of 3-methylthiophene, in anisole was added. The polymerization was allowed to proceed for 2 hours under reflux, followed by the addition of purified MG8. The macromonomer MG8 was allowed to polymerize overnight. The polymerization was terminated by the addition of methanol. The polymers were precipitated into hexanes and finally washed with methanol in a soxhlet extractor.

Measurement and characterization details are available in references 1-4.

In table 1, a series of P[MG8-4VP] block copolymers are listed. The polymers display monomodal molecular weight distribution with reasonably low M_w/M_n (1.1 to 1.3). Thermal studies on the block copolymers show microphase separation as indicated by the presence of two glass transition temperatures. Depending on the block copolymer composition, a soft (oxyethylene) phase glass transition temperature (T_g) is observed between $-60^\circ C$ and $-45^\circ C$ and a hard (4-vinylpyridine) phase T_g between $135^\circ C$ and $142^\circ C$. In these block copolymers, the oligooxyethylene block has been doped with $LiClO_4$ to obtain an ionic conductive phase and the vinylpyridine block (after quaternization) has been doped with 7,7,8,8-tetracyanoquinodimethane (TCNQ) to obtain



Scheme 1 Synthesis of P[MG8-4VP]



Scheme 2 Synthesis of P[3MT-MG8]

Table 1 Weight fraction, glass transition temperature (T_g) and conductivity (σ) of P[MG8-4VP] block copolymer

P[MG8-4VP]	weight 4VP	fraction MG8	T_{g1} (°C)	T_{g2} (°C)	σ (electronic) ^a (S cm ⁻¹)	σ (ionic) ^b (S cm ⁻¹)
#1	0.31	0.69	-60	140	5.7×10^{-8}	7.9×10^{-8}
#2	0.52	0.48	-61	136	3.6×10^{-7}	7.5×10^{-8}
#3	0.61	0.39	-49	135	3.3×10^{-6}	2.1×10^{-8}
#4	0.65	0.35	-55		7.9×10^{-6}	3.1×10^{-8}
#5	0.83	0.17	-45	142	9.2×10^{-8}	3.0×10^{-9}

a). at 30 °C. b). at 30 °C; ethylene oxide/Li⁺ mole ratio of 10

Table 2 Weight fraction, glass transition temperature (T_g) and UV-visible absorption maxima of P[3MT-MG8] block copolymer

P[3MT-MG8]	weight 3MT	fraction MG8	T_{g1} (°C)	T_{g2} (°C)	UV-visible absorption maxima ^a (nm)
#1	0.51	0.49	-55	74	360
#2	0.32	0.68	-55		360
#3	0.27	0.73	-55		355
#4	0.69	0.31	-55	94	376
#5	0.76	0.24			406

a). in CHCl₃

electronic conductive phase. Electronic conductivities and ionic conductivities as high as $3.3 \times 10^{-6} \text{ S cm}^{-1}$ and $7.9 \times 10^{-6} \text{ S cm}^{-1}$, respectively, can be obtained in the doped systems. Detailed electronic properties are available in references 1 and 2. There is a serious drawback with the P[MG8-4VP]/dopant systems. While the ionic conductivity of this system is high, the fact that the electronic conductivities are only in the 10^{-7} to $10^{-6} \text{ S cm}^{-1}$ range at 30°C is a problem. Our targeted applications for these MIEC block copolymers include electrochemical devices which probably will require higher electronic conductivities. Therefore, the P[3MT-MG8] series of polymers were prepared. In these block copolymers, it should be possible to appropriately dope the 3-methylthiophene block and the oligo(oxyethylene) block to obtain electronic conductivities $>10^2 \text{ S cm}^{-1}$ and ionic conductivities around $10^{-5} \text{ S cm}^{-1}$ at 25°C , respectively. In table 2 and 3, a series of block copolymers are listed with their glass transition temperatures, UV-Visible absorption maxima, electronic and ionic conductivity values.

Some of the P[3MT-MG8] polymers show two glass transition temperatures indicating microphase separation. However, in block copolymers containing lower weight fraction of the 3-methylthiophene block, the hard phase T_g is not observable by DSC. More sensitive techniques which allow the observation of smaller microdomains, such as DMTA, may be helpful to understand microphase separation. Currently, the morphological details of these block copolymers are being studied. The P[3MT-MG8] samples are reddish powdery materials and are solution processible. Poly[3-methylthiophene] homopolymers prepared by our method exhibit absorption maxima around 410 nm on the UV-Visible spectrum. P[3MT-MG8] block copolymers show absorption maxima between 355 to 406 nm. Interestingly, the absorption maxima for the P[3MT-MG8] block copolymers are a function of both the weight fractions of 3-methylthiophene and the overall length of segment in the block copolymer. Higher 3-methylthiophene content shifts the absorption maximum to longer wavelength. We believe this reflects the influence of the "interphase" on the effective conjugation of the 3-methylthiophene block. In other words, the fraction of the 3-methylthiophene block present in the interphase will also determine the effective conjugation length. Further work is needed to understand this phenomenon.

The electronic and ionic conductivities of the block copolymers are listed in table 3. In these instances the electronic conductivities were obtained by the four probe method. The ionic and electronic conductivities of the block copolymers are a function of their composition. At 30°C P[3MT-MG8] #2 exhibits an ionic conductivity of $6.6 \times 10^{-7} \text{ S cm}^{-1}$, while copolymers # 4 and 5 displays values $<10^{-9} \text{ S cm}^{-1}$ and may be classified as non-ionic conductors. Therefore, the ionic conducting domains are discontinuous in these

Table 3 Electronic (σ_{ele}) and ionic (σ_{ion}) conductivities of P[3MT-MG8]

P[3MT-MG8]	I ₂ % (by weight)	σ_{ele} (S cm ⁻¹)	σ_{ion} (S cm ⁻¹) ^a
#1	47.2	2.6×10^{-4}	2.6×10^{-7}
#2	44.6	1.2×10^{-4}	6.6×10^{-7}
#3	37.2	5.6×10^{-4}	6.4×10^{-7}
#4	40.9	1.0×10^{-3}	$< 10^{-9}$
#5	50.1	7.6×10^{-4}	$< 10^{-9}$

a). at 30 °C; ethylene oxide/Li⁺ mole ratio of 10

Table 4 Glass transition temperature (T_g), recrystallization temperature (T_c), melting temperature (T_m) and ionic conductivity of PEO/P2VP/LiClO₄ complexes

polymer system	EO/Li ⁺	T_g (°C)	T_c (°C)	T_m (°C)	σ (S cm ⁻¹)
PEO(85)/P2VP (15)/LiClO ₄	5	4			6.3×10^{-6}
	10	-27			1.3×10^{-5}
	15	-39	-10	59	1.1×10^{-5}
	20	-39	14	65	7.6×10^{-6}
	25	-41	15	63	3.6×10^{-6}
PEO(75)/P2VP (25)/LiClO ₄	2	-48			6.0×10^{-6}
	5	-35			3.6×10^{-6}
	10	-41	10	43	1.1×10^{-6}
	15	-35	20	62	6.5×10^{-7}
	20	-34	6	65	2.0×10^{-7}
	25	-40	-11	66	4.8×10^{-7}

two polymers, most likely spherical oligo(oxyethylene) domains immersed in a 3-methylthiophene matrix. The electronic conductivities of the P[3MT-MG8] block copolymers are around 10^{-4} S cm^{-1} to 10^{-3} S cm^{-1} range at 30 $^{\circ}$, with the highest value of 1.0×10^{-3} S cm^{-1} observed for P[3MT-MG8] #4. For all these block copolymers the electronic conductivities are higher than the ionic conductivities, which was one of the goals of this study. Also, the bulk electronic conductivities are quite reasonable. Detailed conductivity measurements are currently underway.

B) Highly Conductive Solid Polymer Electrolytes prepared by Blending High Molecular Weight Commercial Polymers.

The field of solid polymer electrolytes is currently of major technological interest. While a large number of new solid polymer/salt complexes reported are promising materials, but the fact that their preparation requires nontrivial synthetic, crosslinking or blending processes is a serious drawback. Therefore, it is of considerable interest to develop easier methodologies for preparing solid polymer electrolytes with reasonable ionic conductivities, dimensional stability and elastomeric properties. In this regard, with the U.S. Army Research Office support, we have made significant contribution to the field of Solid Polymer Electrolytes - we have developed a methodology for preparing highly ionic conductive polymers with the desired properties by blending high molecular commercial polymers. The thermal and ionic conductivities of some poly(ethylene oxide) (M.W. 600,000)/poly(2-vinylpyridine) (M.W. 200,000)/LiClO₄ blends with 15% and 25% P2VP content. are presented in Table 4. The data indicates that PEO (85% by weight)/P2VP(15 % by weight)/ LiClO₄ blend at an ethylene oxide/Li⁻ mole ratio of 10 exhibits an ionic conductivity value of 1×10^{-5} S cm^{-1} at 25 $^{\circ}$ C and is an elastomeric material with dimensional stability. The data also indicates that the blend with 15% P2VP content exhibits ionic conductivity $> 3.0 \times 10^{-6}$ S cm^{-1} at 25 $^{\circ}$ C over a wide salt concentration range. Therefore, slight variations in the salt concentration, via precipitation or otherwise, will not significantly effect the ionic conductivity and hence the power output of a solid state battery. Overall our research has resulted in the development of several blends of poly(ethyleneoxide)/poly(2-vinylpyridine) or poly(4-vinylpyridine)/LiClO₄, all of which are suitable for application in a variety of electrochemical devices. To the best of our knowledge, we are the first to show the highly ionic conductive (1×10^{-5} S cm^{-1} at 25 $^{\circ}$ C) blends may be prepared with commercially available high molecular weight polymers. Details about these blend systems are available in references 3 and 4.

CONCLUSION

Our research has really developed a new class of electroactive polymers - the MIEC block copolymers. Further research is required understand the properties of the MIEC block copolymers. In particular an understanding of the microstructure and its relation to electronic properties is important. As far as application, the P[3MT-MG8] system is at a stage where they may be tested as the active components in sensors. We plan to start this work soon. Another significant contribution our research is the "methodology of blending" commercial polymers to prepare solid polymer electrolytes that we have developed under the U.S. Army Research Office support. We feel this development will be key to large scale commercialization of high energy density storage devices and the filed of solid polymer electrolytes.

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