REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1. AGENCY USE ONLY (*Leave Blank*)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	11/20/98	Final Report, 4/27/98-10/27/98

4. TITLE AND SUBTITLE
Enzymatically-Catalyzed Polymerization(ECP)-Derived Polymer Electrolyte for Rechargeable Li-Ion Batteries

5. FUNDING NUMBERS
CDAAN02-98-P-8428

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Soldier Systems Command
Acquisition Directorate
attn: AMSSC-AD
Natick, MA 01760-5011

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Approved for Public Release; Distribution Unlimited

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for Public Release; Distribution Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (*Maximum 200 words*)

Report developed under SBIR contract covers the syntheses and electrochemical characterizations of novel polymer electrolytes derived from compounds synthesized via enzyme-catalyzed polymerization(ECP) techniques. A reproducible method was developed to functionalize target monomers via the Mitsunobu reagent, and subsequently polymerizing the modified monomers utilizing enzyme catalytic method. Specifically, polyphenols were reacted with three main types of alcohols in order to establish trends for the incorporation of enhanced ionic conductivity in these materials. The materials synthesized were found to be complex mixtures of derivatized polyphenols which we sought plus coupled polyphenols and coupled alcohols. This molecular complexity maybe beneficial in ensuring that the materials remain amorphous over a broad temperature range. This is an important feature of solid-state polymer electrolyte for battery applications. Functionalization of a biphenol, with subsequent enzyme-catalyzed polymerization, was also attempted and this effort was successful in obtaining samples for polymer film processing and later electrochemcal characterizations. Conductivities of polyphenol-derived polymers were found to be superior to pure PEO, and the materials were found to be electrochemically stable up to 5.0 volt versus Li. The use of inert additives such as Ti02 and Si02 should further enhance the conductivity of the polyphenol-derived polymer electrolyte films.

14. SUBJECT TERMS			15. NUMBER OF PAGES
SBIR REPORT POLYMER ELECTROLYTE Li-Ion Batteries			25
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	

Enzymatically-Catalyzed Polymerization (ECP)-Derived Polymer Electrolyte for Rechargeable Li-Ion Batteries

Contract Number DAAN02-98-P-8428

Phase I Final Report

April 27, 1998 to October 27, 1998

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1.0 Introduction

The premise of our proposal was to determine the feasibility of preparing novel materials derived from compounds synthesized via enzyme-catalyzed polymerization (ECP) techniques and, further, to determine their potential for battery applications. The initial plan involved the etherification of a number of ECP-derived polyphenols (Figure 1) with a series of 3 main types of alcohols (Figure 2). Our goals were to establish trends for the incorporation of enhanced ionic conductivity in these materials in order to (1) thereby demonstrate a correlation between specific structural additions and the ability to manipulate conductivity in polymers, and (2) to make working (rechargeable type) batteries from these new materials.

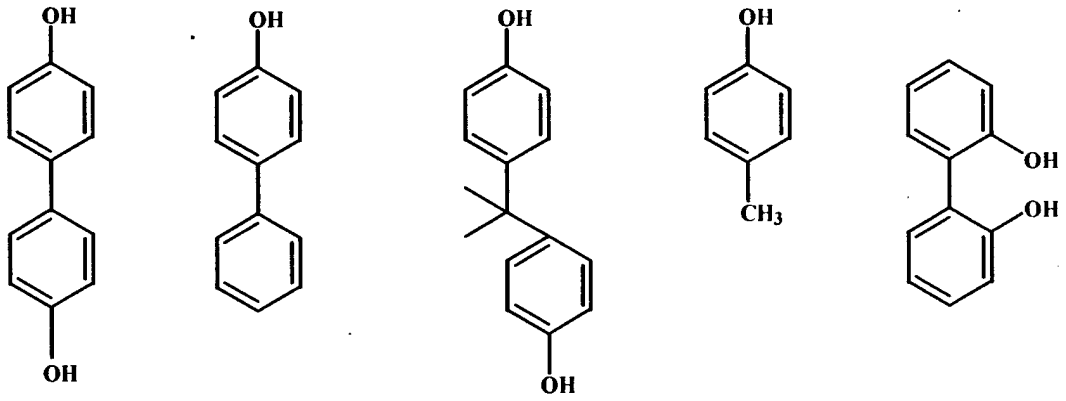
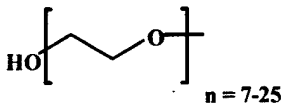


Figure 1.

The main thrust of the synthetic portion of this program was to employ the Mitsunobu etherification reaction to "connect" alcohols possessing the structural features of these three types to an ECP-type polyphenol. Initially, these synthetic connections were attempted between the ECP polymer and several variants of Type 1: poly(ethylene glycol) (of varying average molecular weights) and poly(ethylene glycol)methyl ether (PEGMEO) (also of varying average molecular weights). In addition, the Type 2 structure depicted in Figure 2 was prepared, and several trials of the etherification reaction attempted.



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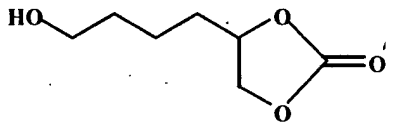

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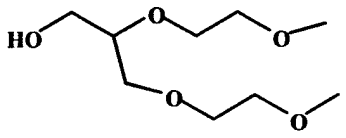


Type 3

Figure 2.

All of the compounds depicted in Figure 1 have been utilized in attempted polymerizations by enzyme-catalyzed oxidative coupling. In addition, our first synthetic attempts at etherification involved the subsequent reaction of Type 1 and Type 2 alcohols with poly(*p*-phenylphenol), poly(bisphenol A), and poly(*p*-cresol) under a variety of conditions. Temperature, solvent, concentration of reactants etc. were varied in vigorous attempts to isolate products of the type shown in Figure 3.

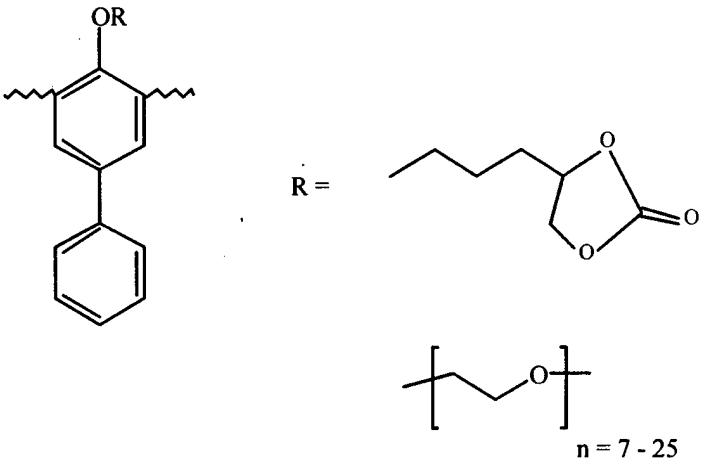
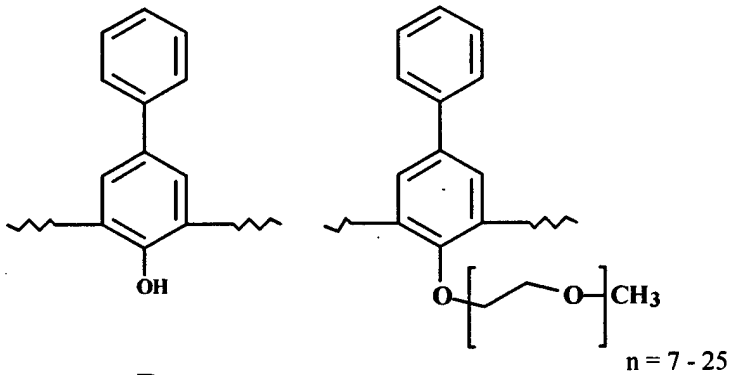
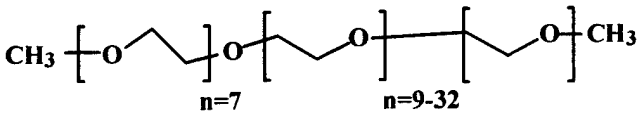


Figure 3.

Yields of product were low to moderate, calculations of yield were based on viscous material obtained after extractions and attempted distillations, so that these materials were predominantly isolated as a series of viscous oils. NMR results were inconclusive in demonstrating that we had formed the ether derivatives; IR was also inconclusive, the humidity of our climate and likely presence of unreacted alcohol negating any inferences that might be drawn from the presence of an O-H stretching vibration at 3650-3584 cm^{-1} [1]. High resolution electrospray mass spec was utilized for three samples, poly(*p*-phenylphenol), **VI** , and **VIII** (See Figure 4).



D VI



VIII

Figure 4.

Based on the conclusions drawn from the results of the mass spec data accrual, a different approach was developed. We believed that functionalization of a biphenol, with subsequent enzyme-catalyzed polymerization would provide the type of structure we required. Our rationale was that if a careful consideration of reaction stoichiometry was maintained, we could etherify one phenolic hydroxyl group, leaving one hydroxyl available for the oxidative coupling reaction.

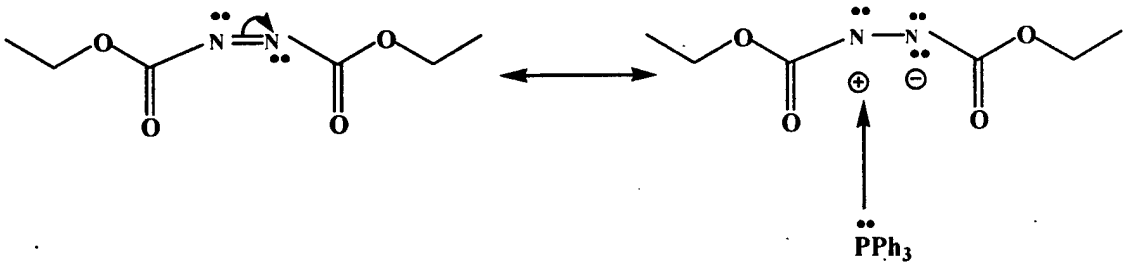
Electrochemical evaluations include the conductivity measurements of three types of polymer films and their stability window. In addition, a preliminary carbonization of polyphenols demonstrates a stable reversible output.

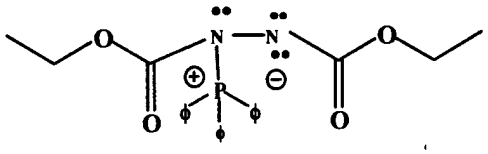
2.0 Results and Discussion

2.1 Synthesis of Polymers

(1). DEAD-Mitsunobu Reaction

The mechanism for the DEAD-Mitsunobu reaction shown in **Scheme I** below. At VCU we are able to isolate one of the by-products of this synthesis from the reaction flask as white needles, possessing a sharp melting point identical to the literature values of 1,2-dicarbethoxyhydrazine[2] (m.p. = 135° C).





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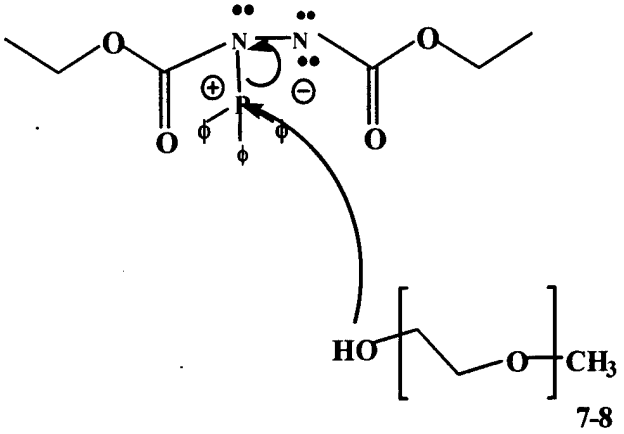

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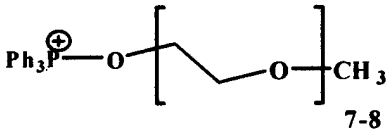


7-8

II

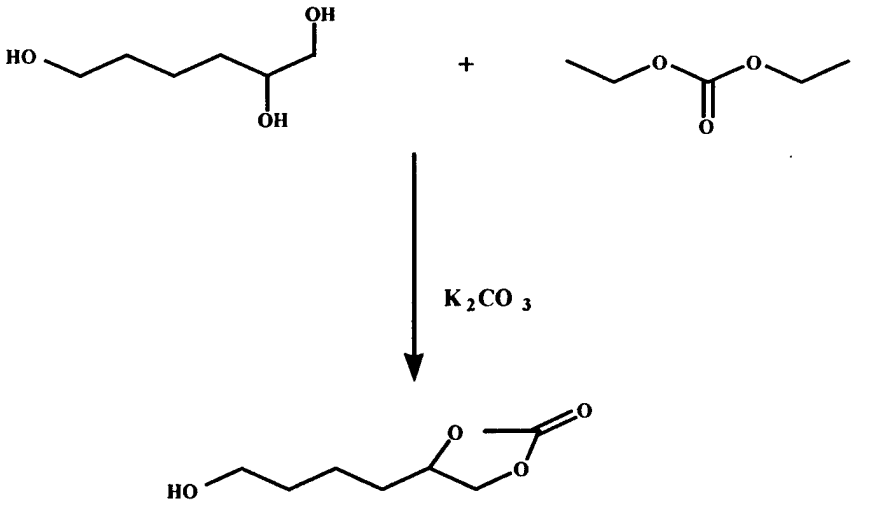
Scheme I.

The structure **I**, is a quaternary phosphonium salt believed to be an intermediate in these types of reactions[3] that is also a Lewis base, potentially capable of abstracting a proton from the two reacting alcohols. In the case of our syntheses, a phenol polymer and the terminal hydroxyl of PEGMEO are the sources of acidic protons. We believe that the phenolate anion (resonance stabilized and predictably derived from the more acidic phenolic alcohol) will not attack the phosphorus as rapidly as that of the linear alkanol, PEGMEO, which by nucleophilic substitution at the phosphorus (the triphenylphoshine group is a relatively good leaving group) should yield the intermediate **II**.

Nucleophilic attack on **II** by the phenol or phenolate anion occurs at the carbon alpha to the triphenylphosphonium leaving group, to yield the target ether. In the course of this reaction, the azodicarboxylate is reduced to the hydrazine

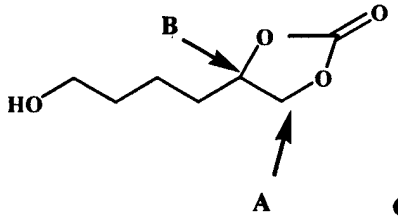
(2). Preparation of Cyclic Carbonate Alcohol, Compound 4

Synthesis, purification, and scale-up were carried out for this compound[4]. The synthesis is depicted in **Scheme II**. Yields remain relatively low, and purification was attempted by Kugelrohr distillation and subsequent vacuum distillation However, a Mitsunobu synthesis with this alcohol and **D** was attempted in THF, and was unsuccessful, there was little indication of any reaction at all, manifested by the absence of heat and color change. Subsequent NMR analysis of the crude material showed resonances for all of the starting materials.



Scheme II
Preparation of 4

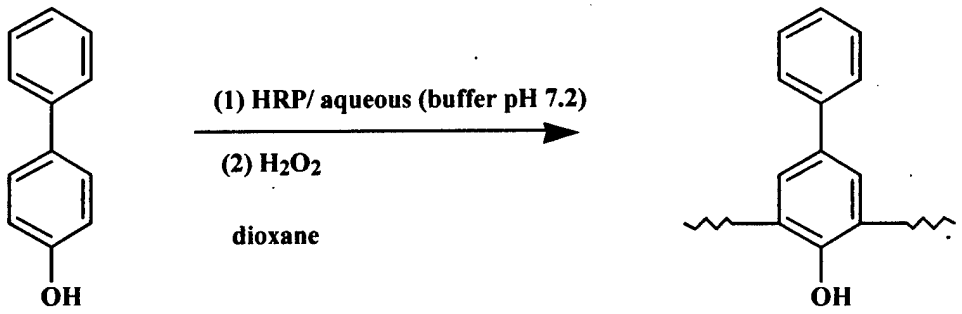
The liquid product's proton NMR shows prodigious amounts of diethyl carbonate still unreacted, but also shows product formation, based on the proton assignments of Wnek *et.al.* [1] for their compounds. In particular, the resonances at 4.6 ppm (1H, triplet) and 4.1ppm (2H, doublet) for protons B and A respectively are clearly absent in the starting materials, and coincide well with reported values for other cyclic carbonate structures (4.08 ppm and 4.52 respectively).



Compound 4

(3). Preparation of Enzyme-Catalyzed Poly(*p*-phenylphenol), Compound D

The synthesis of **D** was carried out as noted in Reference 11. **Scheme III** shows the reaction. Enzyme concentrations were maintained at approximately 0.5 mg/mL and the monomer was introduced to the aqueous enzyme mixture in dioxane. Concentrations of monomer and hydrogen peroxide were approximately 0.1 M. The enzyme solution was buffered using HEPES buffer in one run and phosphate buffer in another. The pH of the solution was buffered at physiological pH for both runs. Reaction mixtures were stirred for approximately 24 hours for each run. Upon addition of hydrogen peroxide to the enzyme/monomer solution, immediate color change was observed to a dark, almost black solution. Recovery of polymer was initially attempted by vacuum filtration of the reaction solution, which, during the 24-hour interval, showed evidence of significant precipitation. However, this proved to be decidedly ineffectual, as material proved too thick to be filtered. Centrifugation was carried out on several batches of material, followed by a water wash. Subsequent centrifugations of decant also provided copious amounts of solid of increasingly lighter color and somewhat lower melting point. We believe these represent lower molecular weight polymer and oligomers. Colors range from a dark green/brown, to brown, to light brown.

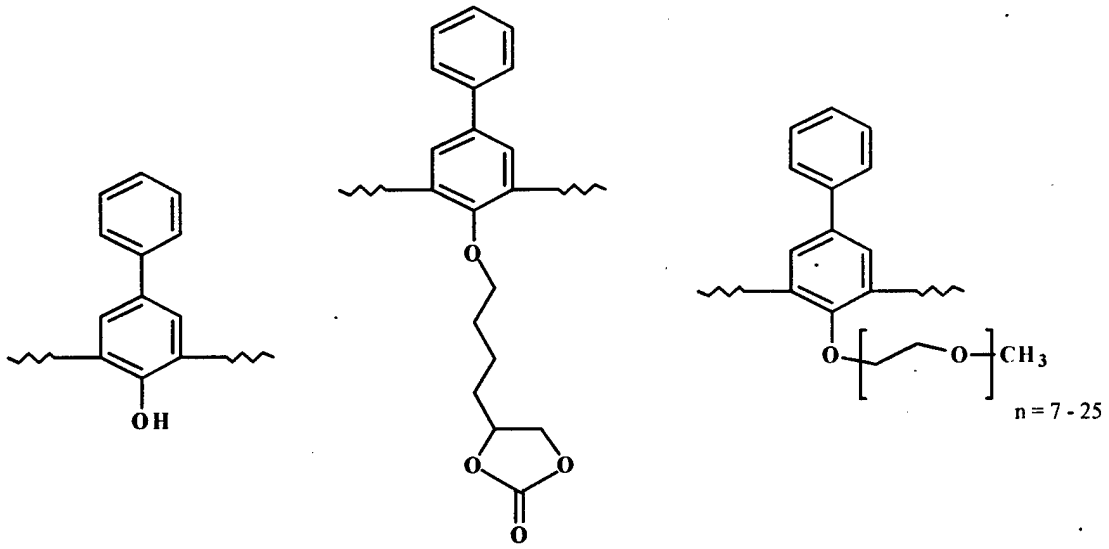


D

Scheme III

(4). Attempted Synthesis of IV

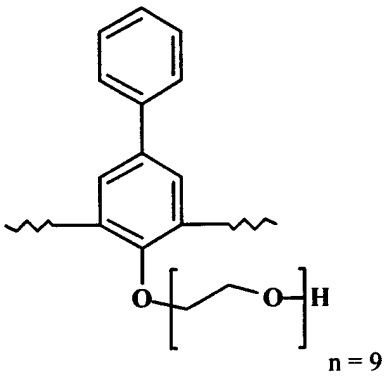
As indicated in the section describing the preparation of compound **4** (**Scheme II**), the Mitsunobu reaction was performed in THF to attempt etherification of the polymer **D** with this compound. No reaction by-products such as 1,2-dicarbethoxyhydrazine or triphenylphosphine oxide were isolated nor detected in the NMR. All evidence supports complete lack of reactivity using these starting materials.



D **IV** **VI**

(5). Synthesis of Compound VII

Numerous trials of the Mitsunobu synthesis have been attempted on the ECP-derived polymers poly(*p*-phenylphenol), poly(bisphenol A), and poly(*p*-cresol) with alcohols of the Type 1 category[5, 6]. Several attempts were made to vary the molecular weights of the alcohol, with the hope of successfully completing a series of products based on these linear alcohol structures. Our first success came in the preparation of compound **VII** (structure shown below). The reaction was done neat, and a sample procedure follows:



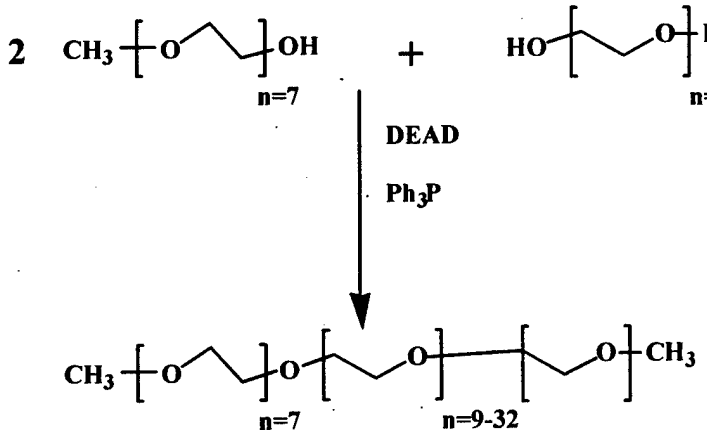
VII

Poly(*p*-phenylphenol) [PPP] (1.0 g, 5.95 mmol), was placed in a 250 mL beaker on a hot plate with stir bar and gently warmed and melted. Poly(ethylene glycol) [PEG] Mn = 400 g/mol (number average molecular weight) was added slowly (1.69 g, 4.22 mmol) so that a homogeneous solution was obtained. To this solution was added diethyl azodicarboxylate [DEAD](1.03 g, 5.95 mmol) and triphenylphosphine (1.56 g, 5.95 mmol). An immediate exothermic reaction took place. The reaction mixture was allowed to cool to room temperature, the greatly increased viscosity of the mixture precluded further stirring.

Conductivity measurements of Compound **VII** was conducted at MaxPower (see results on **Electrochemical Evaluations**). There are indications that this material will be suitable for the proposed applications. Our NMR characterization of this material, as in numerous trials preceding this synthesis, suggests the formation of the ether (observance of downfield shift of methylene protons from the Type 1 alcohol), and in each case, evidence of the 1,2-dicarbethoxy hydrazine (6 H, t, δ 1.15 ppm and 4H, q, δ 4.05 ppm) has been clearly manifested in the crude reaction mixture. However, numerous concerns regarding the DEAD reaction have been raised, despite literature support for the feasibility of etherifying phenols with 1° and 2° alcohols[7, 8, 9].

We have postulated, then, based on experiments we carried out using the DEAD reaction on two linear polymeric alcohols, that there is something unique about attempting this synthesis with the ECP-derived polyphenols. The DEAD reaction was done using PEG (Mn=400) and a low molecular weight PEGMEO (poly(ethylene glycol)methyl ether)

(Mn= 350) and a second trial with high molecular weight PEG (Mn = 1500). The reaction is depicted in Scheme IV.



VIII

Scheme IV.

Mass spec data confirm the presence of species with molecular weights greater than 1800 g/mol. In addition, spacings of 44 daltons are observed throughout. The NMR of the DEAD product of this reaction shows a sharp singlet in the methylene region, suggesting that all the methylene protons are equivalent. The signal also appears downfield in both the low and high molecular weight trials. Further evidence to support the structure for **VIII** is observed in the integrations for methylene protons to methyl protons. In the low molecular weight version, the signals integrate to roughly 16 methylenes to 1 methyl proton, which appears to confirm the structure in this case. For PEG (Mn=1500), the integrations also appear to confirm the structure, with a ratio of 33 equivalent methylene protons to 1 methyl proton. We believe we can conclude from these data, together with the increased viscosity of the mixture, that etherification via the Mitsunobu synthesis has been successful in this case.

What are the possible effects contributing to the difficulties seen in the reaction when utilizing polyphenols and linear alcohols? The mass spec data on **VI** seem to suggest that the value for n is in fact 2, not 7. A mass difference of 278 daltons is observed in the three peaks of highest intensity, 579, 857, and 1135. This lends support to a repeating unit that contains a much shorter chain linear alcohol, and further appears to add support to its attachment. We propose that the problem here is the competition for OH sites, and that the larger molecular weight linear Type 1 alcohols are at a disadvantage in terms of competition with phenol sites on other chains in solution and very short chain oligomers of PEG and PEGMEO. This is based on the premise that PEG and PEGMEO will assume a random coil orientation in solution[10]. For PEGMEO, the single reactive site may be "buried" within the coil (See Figure 5).

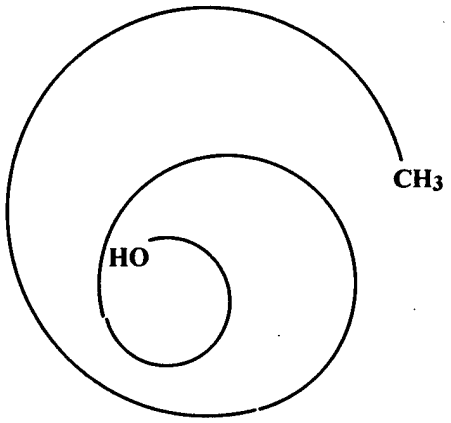


Figure 5.

Such a conformation will significantly reduce the availability of the reactive site relative to those active sites on rigid ECP-polyphenol backbones or those on linear, short chain oligomers of PEG or PEGMEO. The formation of alternate structures as depicted in Figure 6 are indicated as a result of this competition.

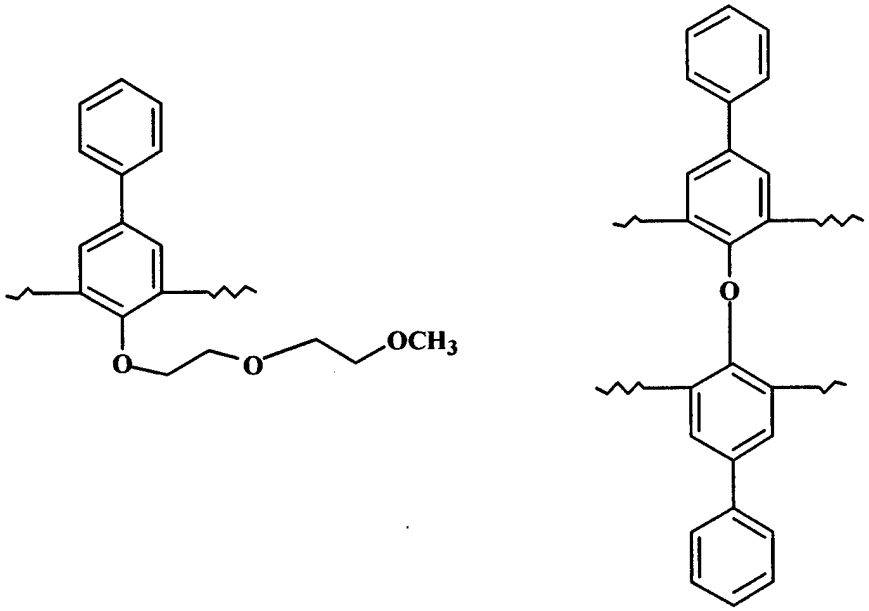
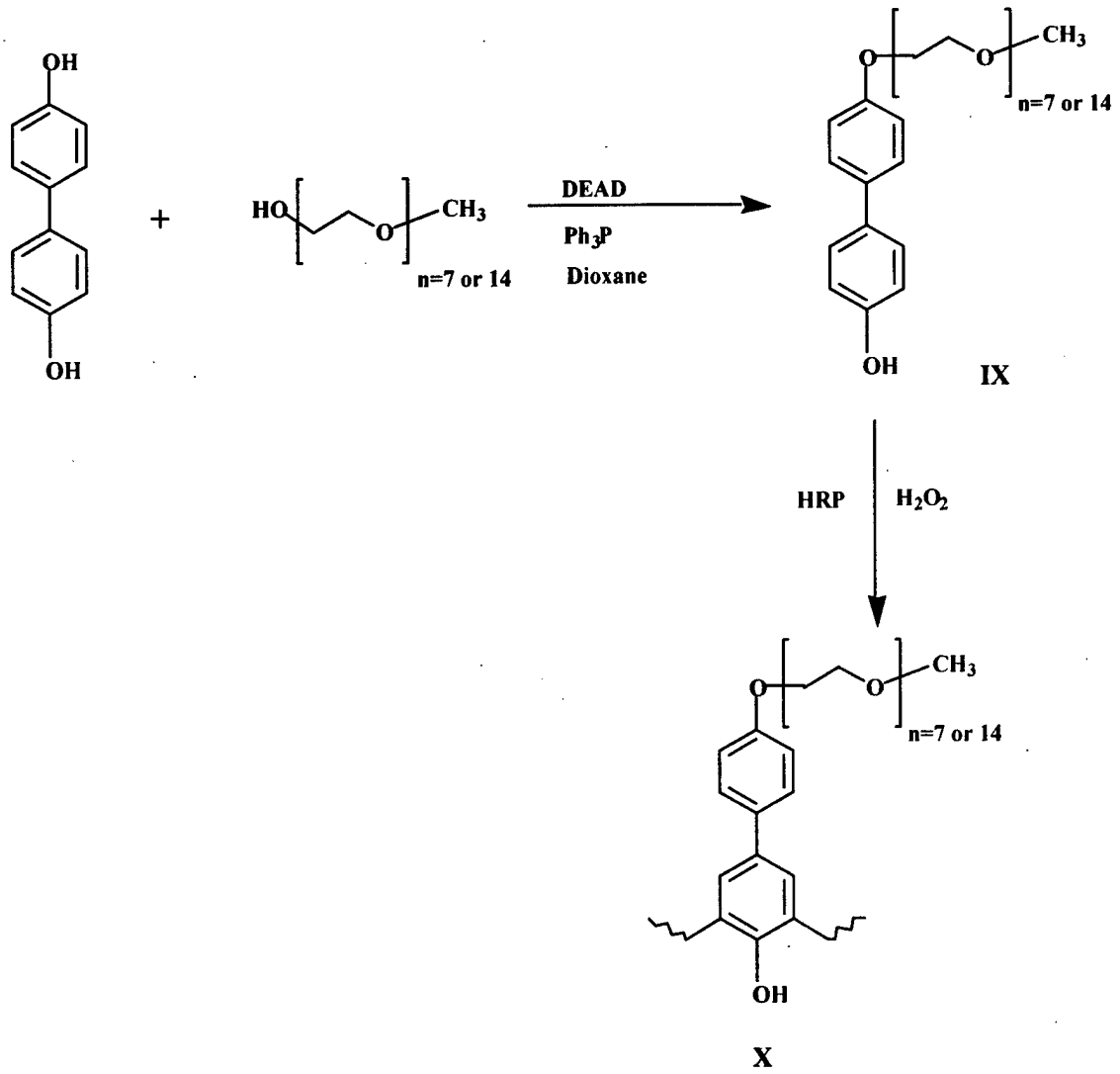


Figure 6.

The rigidity of the polyphenol permits it to present its hydroxyl groups to one side of an adjacent polymer chain, and there are 5-7 such sites per chain. The short-chain (n = 2) PEGMEO oligomer has no substantive "coil", making its hydroxyl group more accessible to reaction.

(6). Preparation of Compound X

In an effort, therefore, to circumvent the complication mentioned above, the following sequence has been attempted (Scheme V):



Scheme V.

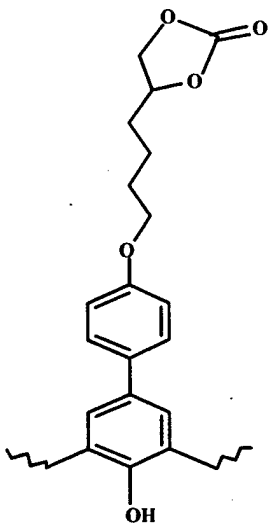
The compound **X**, can be cast as a film from dioxane, and samples of this compound have been sent to MaxPower for conductivity testing. As indicated in the introduction of this report, the physical properties of this material are superior to previous products. We believe that we have minimized competition for hydroxyl sites by a second ECP-chain by carrying out the DEAD reaction on the monomer in solution. A marked increase in viscosity characterized the conversion of the monomer to the PEGMEO functionalized compound, and another marked increase in viscosity characterized the conversion of this material to the polymer. A typical synthetic procedure follows:

Preparation of IX: A 250 mL round-bottomed flask was charged with 4, 4'-bisphenol (5.0 g, 2.7 x 10^{-2} mol) in approximately 25 mL of dioxane. Poly(ethylene glycol)methyl ether (9.40 g, 2.69 x 10^{-2} mol) was added to flask and the mixture was warmed gently. Diethylazodicarboxylate (4.69 g, 2.69x10^{-2} mol) was added to the solution with stirring. A solution of triphenylphosphine (7.06 g, 2.69x10^{-2} mol) in approximately 30 mL of dioxane was added to the reaction mixture with immediate color change and heat evolution. The mixture was stirred for 18 hours. Removed solvent and dissolved residue in methylene chloride, followed with an aqueous extraction and evaporated organic layer to an amber, viscous oil. Yield = 11.6 g (84.7%).

Preparation of X: Monomer **IX** (11.6 g, 2.28 x 10^{-2} mol) was placed in a 250 mL round-bottomed flask with 171 mL of dioxane (representing 75% of a 228 mL total solution volume). Horseradish peroxidase (Type II) (114 mg, for final solution mass of 0.5 mg/mL solution) was dissolved in 57 mL of HEPES buffer (pH=7.5) and added to the monomer solution slowly. Hydrogen peroxide (30% w/w) was added to give a 0.1 M H_2O_2 solution (2.58 g) and an immediate color change took place to inky black. The mixture was stirred for 18 hours. The reaction solution was centrifuged at 6000 rpm for 20 minutes and gel-like solids washed with water and dried. Product material was taken up in dioxane and cast on microsope slides, a transparent, somewhat tacky film was obtained.

(7). Preparation of XII

Our work on preparing derivatives of Type 2 alcohols has not previously been successful, however, we have attempted to prepare the compound **XII** (shown below) by the alternate method described above, that of enzyme-catalyzed polymerization after formation of an etherified monomer.



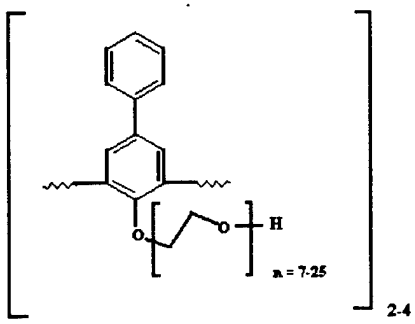
XII

The results of this synthesis are pending, we hope to assess the efficacy of our approach with respect to the Type 2 alcohol.

2.2 Electrochemical Evaluation

(1). Conductivity Measurements

We evaluated a sample of the polymer poly(poly(ethylene glycol)biphenyl ether) whose molecular formula is:



The polymer is yellow-brown and has a tendency to become fluid at around 50°C. In order to ascertain the suitability of this compound for the preparation of a polymeric electrolyte we dissolved a lithium salt in the polymer, namely Li-triflate, which is widely used in lithium battery research. The molar ratio utilized (salt to polymer) was, initially, 1 mole of lithium for each monomer unit and subsequently reduced to half this value. As a preliminary approach to studying this new material, we followed two preparation routes. (a) Solid State High Temperature Solubilization (SSHS) which consists of liquefying the polymer by heating to 80-90°C, and then adding the salt (this sample will be referred thereafter as the sample ***S***). (b) Low Temperature Solvent Assisted Solubilization (LTSAS) where both the polymer and the salt are dissolved in a common solvent (typically THF or acetonitrile) followed by casting the solution onto a Teflon sheet, slowly allowing the solvent to evaporate, and finally drying the resulting polymeric film at 40°C under vacuum. The LTSAS membranes are referred to as sample ***V***.

All manipulations for preparation of samples ***S*** and ***V*** were carried out in an ultra-dry environment. Furthermore, in order to determine if we could significantly improve the conductivity of the sample ***S***, we prepared another membrane by adding a plasticizer to this sample. This was accomplished by adding a drop of the well known, high-dielectric constant, plasticizing mixture EC/PC (50:50) to sample ***S***. This new polymer membrane is referred to as sample ***E***.

The conductivities of the samples were measured by sandwiching the membranes between two identical stainless steel (SS) blocking electrodes whose surfaces were previously polished to metallographic grade using an alumina paste. The conductivities were measured with a Solartron 1255 FRA coupled to a Solartron 1286 potentiostat in a two-electrode configuration.

Figure 7 shows a typical impedance spectrum taken at 25°C for sample *V*. The spectrum is characteristic of an ionic conducting material in contact with blocking electrodes. The spectrum shows a low frequency spike associated with a high frequency semicircle. The blocking (toward the reaction $Li \rightarrow Li^+ + 1e^-$) nature of the electrodes is clearly evidenced by the tendency of the spike toward infinitive imaginary values of impedance as the frequency tends to zero. This part of the spectra can thus be identified with a simple capacitance due to the electrical double layer which forms at the interfaces of the polymer electrolyte and the SS electrodes (see the equivalent circuit shown in Fig. 7). The charge transfer resistance associated with the double layer capacitance, being infinite (blocking behavior) is revealed by this part of the spectrum. A high frequency semicircle is observed in the range 1 kHz - 100 kHz. This is the region where the ionic conductivity of the bulk material is the only contribution to the overall impedance. This semicircle is simulated by the parallel combination of Rel and Cg which are, respectively, the bulk resistance of the ionic conductor and geometrical capacity of the cell. This latter capacitance is simply the capacitance of a capacitor formed by the two parallels SS electrodes with the polymeric sample acting as the dielectric media. In order to determine the best values for these parameters, we have utilized the Non-Linear Least Square Fitting program written by B. Boukamp of the University of Twente, Holland. From Rel, it is possible to calculate the conductivity of our samples by the formula:

$\text{sigma}/\ \text{Ohm}^{-1}\ \text{cm}^{-1} = (1/\text{Rel})*(l/S)$

where 'l' is the distance between the electrodes and 'S' their surface area expressed, respectively, in units of cm and cm^2.

Analogously, utilizing the measured values of Cg, the 'dielectric constant' of the dielectric medium (the polymer electrolyte membrane) can be calculated from the equations:

$Cg = \varepsilon r * (l/S)$

$Co = \varepsilon o * (l/S)$

$Er = Cg/Co$

where εr and εo are the permittivities of the polymeric material and of the vacuum, respectively, and *Er* is the *relative* dielectric constant of the polymer membrane.

Inspection of all the spectra leads us to the first important conclusion that these polymer electrolytes do not possess any electronic conductivity. In fact, the low frequency spike is always pointing towards infinity for the imaginary part of the impedance as the frequency tends to zero (d.c. current). If a sample does exhibit electronic conductivity, the low frequency spike would show a finite (real) impedance value on the real axis at zero frequency. From a molecular point of view this experimental evidence implies that there is neither 'long distance overlapping' of the external molecular orbitals in the polymer

nor there is any jumping (tunneling) possibility for electron transfer. In other words, these membranes do indeed exhibit ionic conductivity, but not electronic conductivity.

Fig. 8 shows the Arrhenius plot of the conductivity of the sample ***S*** in the temperature range between 20 and 90°C. It is evident that all the experimental points can be fitted by a simple linear regression which is characteristic of a solid electrolyte in which the mobile ions move surrounded by a fixed amorphous environment or by an ordered lattice. Typical are the glasses for the first class, and ceramic electrolytes for the second. The ions in these latter cases can move only by jumping between localized sites, and there is no contribution to ionic movement from the polymer network. Thus, we might infer that from a molecular point of view, in our sample the polymeric chains are mainly *immobilized* in a rigid entangled configuration. This hypothesis is not surprising when we consider both the presence on the chains of phenolic OH groups which can result in intra and intermolecular H-bonding, and the steric hindrance of the aromatic groups.

Fig. 9 reports the dielectric constant of sample ***S*** as function of temperature. The data appear quite scattered and this phenomenon can be attributed to the higher errors associated with the values of Cg as the temperature increases. In fact, as the temperature increases, the sample resistance decreases and the maximum of the high frequency semicircle shifts towards higher and higher frequencies. This is due to the fact that our experimental apparatus is limited to 100 kHz while the fitting program is programmed to extrapolate to infinite high frequency utilizing a decreasing number of experimental points. However at 25°C the spectrum (Fig. 7) is completely resolved within the accessible experimental frequency range, and the measured value 58 for *Er* at this temperature can be considered quite accurate. Noting that for polyethylene oxide (PEO), *Er* values reported in the literature range between 3 and 5, it appears surprising that our polymer shows an *Er* value one order of magnitude higher. From a practical point of view this is a beneficial property, as a higher dielectric constant of the host polymer helps in dissociating the dissolved salt and in reducing ion pair formation. From a molecular point of view this experimental evidence implies a higher value of the polymer moiety dipole moment and/or larger chain entanglement.

Fig. 10 shows the dielectric constant of the sample ***E*** that has the same salt/polymer mole ratio as sample ***S,*** but has been plasticized by an EC/PC (50:50) solvent mixture. Fig. 11 shows the Arrhenius plot of the sample ***E***. As evident from this figure, the data points can not be fitted to a linear smoothing equation, but rather are curved which can be fitted to a concaved smoothing equation. This behavior is characteristic of liquid electrolytes where the ions move in a mobile framework that contributes to the overall conductivity. As the temperature decreases the viscosity of the medium becomes more and more important and the conductivity decrease is higher than that expected from the activation energy alone. In our case the solvents seem to have plasticized the polymer and consequently the more flexible chains can now contribute to enhanced ionic mobility. The dielectric constant measured at 25°C is 98. This value is in agreement, within experimental error, to the sum of the average value, 75, to be considered for the mixture

EC/PC and the average value of the first two points of Fig. 9. The sudden decrease of E_r observed at higher temperatures can reasonably be attributed to some loss of the solvent mixture and more likely to the breaking of intra and intermolecular H-bonds.

Fig. 12 shows the Arrhenius behavior of the sample ***V***. Similar to the behavior of sample ***E***, sample ***V*** shows non-linear (concave) Arrhenius behavior. Moreover, the conductivity of this sample is higher than that of the other two samples over the entire temperature range. This experimental evidence leads us to conclude that the polymer sample ***V*** also has flexible polymer chains which aids (enhances) ionic conductivity. Since no plasticizers were added to polymer sample ***V***, it is probable that the enhanced conductivity is due residual THF bonded to the polymer groups or solvating the lithium ions. This hypothesis is coherent with the observed increase of the conductivity of the sample ***V*** with respect to samples ***S*** and ***E***. Furthermore the deviation of the point at the highest temperature can be ascribed to some loss of the residual THF during the measurement. The sudden drop of the ***Er*** values, exhibited by both the plasticized samples ***E*** and ***V*** (Figs. 10 and 13), is not evident in the case of sample ***S*** (Fig 9). This appears to indicate a probable change in the structure of the molecular dipoles in the polymeric electrolyte with a relaxation to a lower energy configuration. This transition being favored in the case of the sample ***E*** and ***V*** which, due to the plasticization, have more flexible chains than the sample ***S***.

Finally, Fig. 14 show for comparison the Arrhenius traces of both the sample S and the standard $(PEO)_8LiClO_4$. It is worth noting two main features. First, the sample S has a conductivity of the same order of magnitude of the conductivity of the PEO sample. Second, PEO the curve shows a break point at 60°C with a sudden change of the conductivity. This inflection point is related to the crystallization of the PEO at this temperature. In the case of the sample S the curve maintains its slope for the entire temperature range and at temperatures lower than 60°C the conductivity of the samples S become higher than that of the PEO. At molecular level this means that the sample S maintain its more conducting amorphous state even at room temperature. To study the effect of salt concentration, sample S was measured for its conductivity at reduced $LiPF_6$ concentration. This result is also shown in Figure 14. In this plot, we also show the positive effect of nano-scale TiO_2 on PEO conductivity. This effective is dramatic, and we will evaluate for the same synergism (if any) on the polyphenol polymers in the Phase II study.

An important finding in our initial electrochemical studies is that the polymers appear to be insulators, i.e. electronic conductivity is not observed. This property is important since any practical device based on polymer electrolytes must not be electronically conductive since this would result in 'shorting' of the cell resulting in poor shelf and cycle life. Moreover another important finding has been that the polymers maintain their more conductive amorphous state all over the temperature range investigated.

While the conductivities of the polymer membranes ***S***, ***V*** and ***E*** are low at ambient temperatures, but they are still much higher than that of the pure PEO at the same

temperature. Our initial electrochemical studies are promising in the sense that they indicate a number of areas to be pursued to increase conductivities over a wide temperature range. We have established techniques for preparing three types of membranes which will be used in future R&D on new polyphenol polymers with increased chain length, replacing the phenolic group with alkyl groups (namely CH_3), and studying the effects of varying salt concentration. Replacement of the phenolic group with an alkyl will probably reduce the dielectric constant of the polymer, but this would be compensated by increasing chain length and a higher mobility for the lithium cation. Furthermore, it is our opinion that we might be able to improve the conductivity of all our samples by preparing composite electrolytes through the addition electrolytes through the addition of nanoscale inert powders.

(2). Electrochemical Stability Window

In order to ascertain the suitability of our in electrochemical couples based on high voltage cathodes we have run a voltammetric linear scan on the cell:

Li/ Sample S/ SS

starting from the OCV and ending at 6 V vs Li/Li^+ couple. The curve in Fig. 15 shows that the electrolyte is stable up to 5 V with a very low electrolytic current.

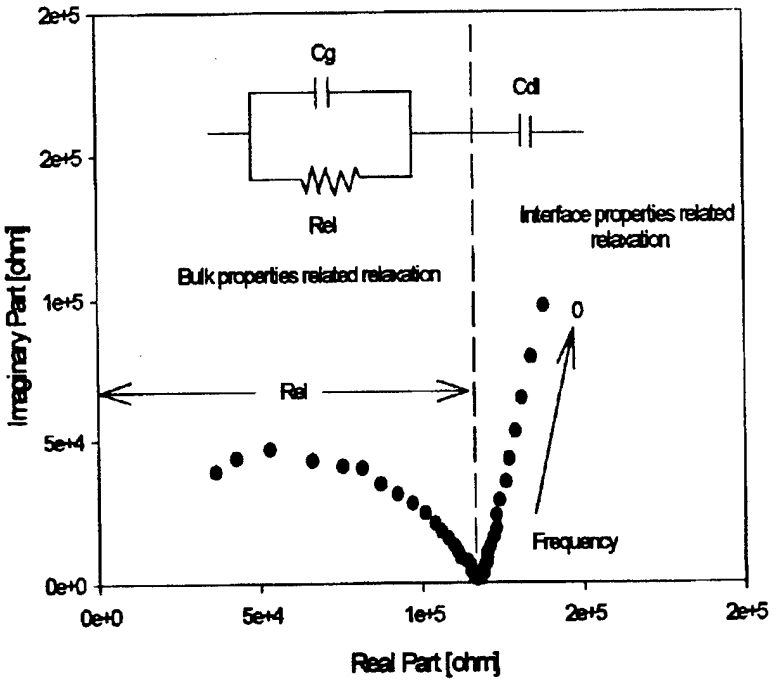


Figure 7. Impedance spectra of sample *V*. $t/°C = 25, f_{min} = 1$ Hz, $f_{max} = 1 \cdot 10^5$ Hz.

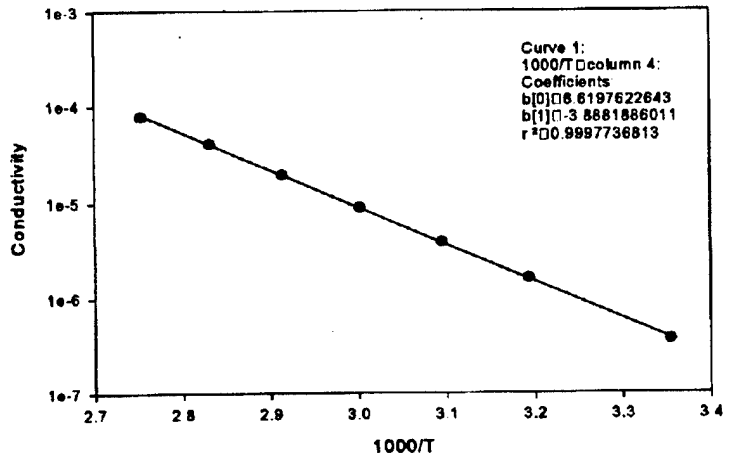


Figure 8. Conductivity of Sample *S* as a function of temperature.

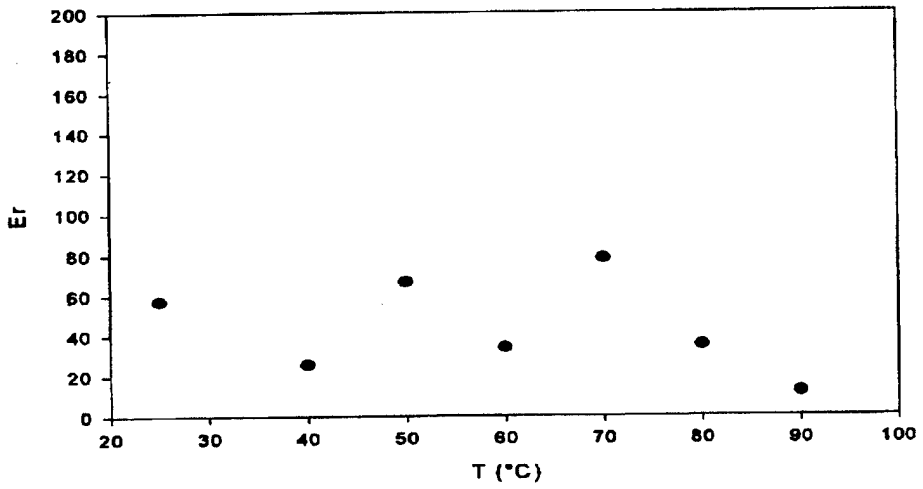


Figure 9. Dielectric constant of sample *S* as a function of temperature.

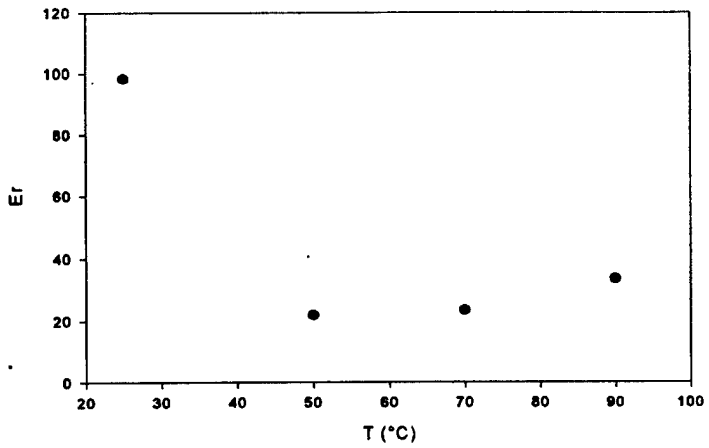


Figure 10. Dielectric constant of sample *E* as a function of temperature

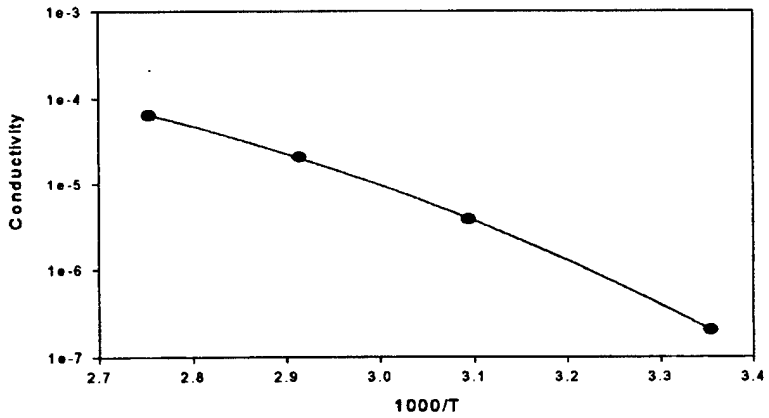


Figure 11. Same polyphenol as sample *S* but plasticized with EC/PC (this is sample *E*)

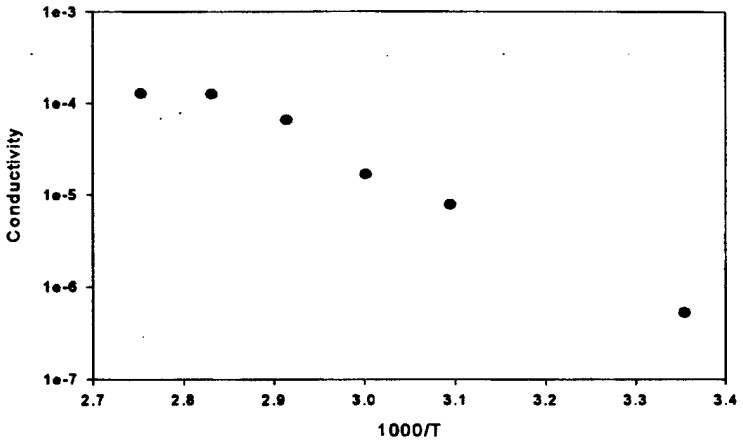


Figure 12. Conductivity of polyphenol sample *V* as a function of temperature.

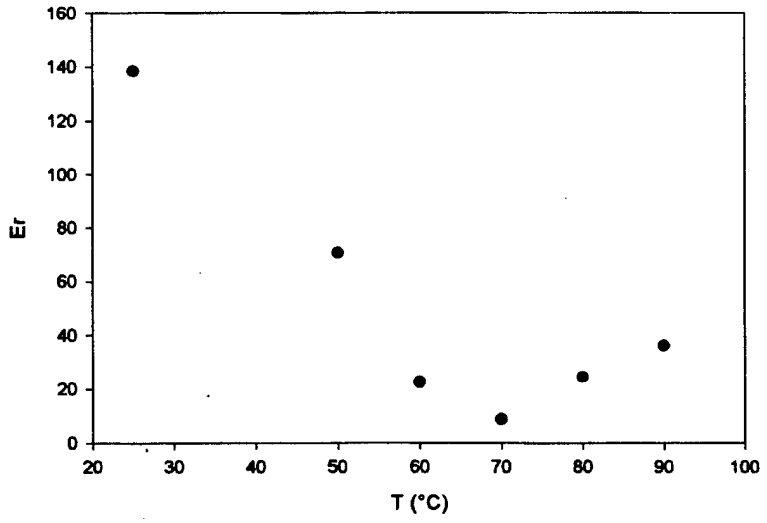


Figure 13. Dielectric constant vs temperature for polyphenol sample *V*.

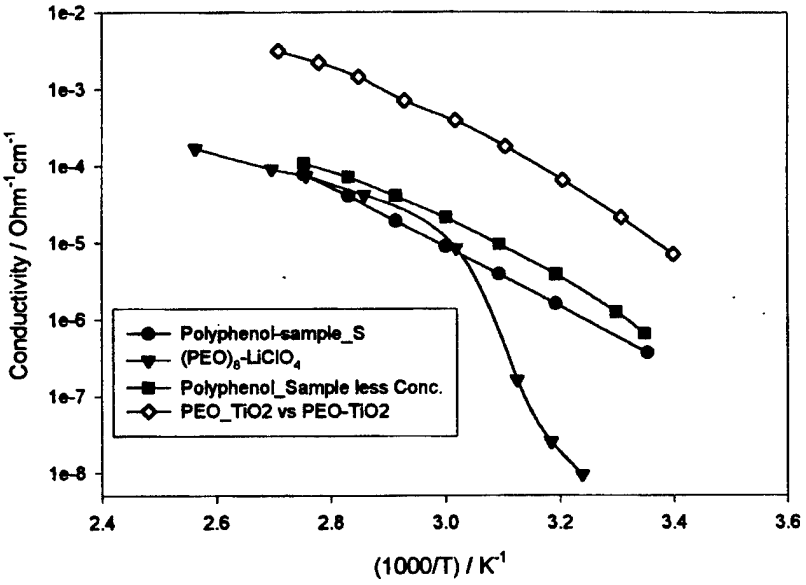


Figure 14. Conductivity comparisons between polyphenols, $(PEO)_8LiClO_4$ and $(PEO)_8LiClO_4 + TiO_2$

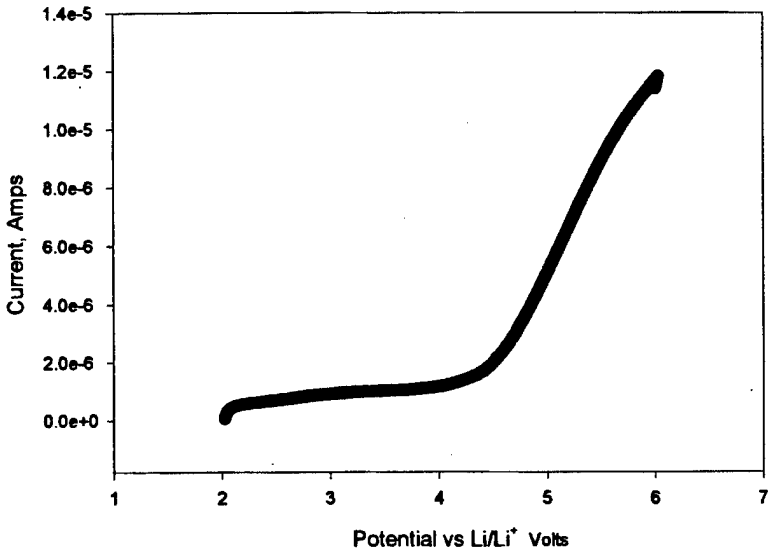


Figure 15. Electrochemical stability window for polyphenol sample *S*.

2.3 Carbonization of Polyphenols

Polyphenol resins as supplied by Schenectady International were pyrolyzed in order to determine if these resins can be used as potential precusor for Li-based anode materials. In a nitrogen environment, the micronized resins (sieved to –270 mesh) was heated to 250^{0}C and held at this temperature for 5 hours. This is the structural stabilization step. The material was then heated in an argon atmosphere to either 500^{0}C or 1000^{0}C and held at this level for one hour. Cool down was conducted at the rate of 4^{0}C per minute.

Achieved yield was 25% and the pyrolyzed product was a shiny and hard porous cake. A soft-sealed pouch cell was used to house the Li/Polyphenol-based carbon cell. The cell was charged and discharged at 0.50mA/cm^2 using a voltage window of 1.50-0.010 volt. Electrolyte solution used was 1.0M $LiPF_6$/EC:DMC:DEC (50:40:10 wt ratio). Surprisingly, even though the irreversible capacity is very high, the material exhibited extremely high initial capacity and good reversible capacity at around 150 (mAh/g). Cycle performance of this material is presented in the attachment as Figure 16. While the irreversible capacity is quite large (about 400 mAh/g which is similar to disordered carbons prepared from sugar, cotton and PAN precursors), what is encouraging that after this intial capacity loss, our carbons cycle very well with constant reversible capacities between 150 mAh/g (the 500°C treated sample) and 130 mAh/g (the 1000°C treated sample).

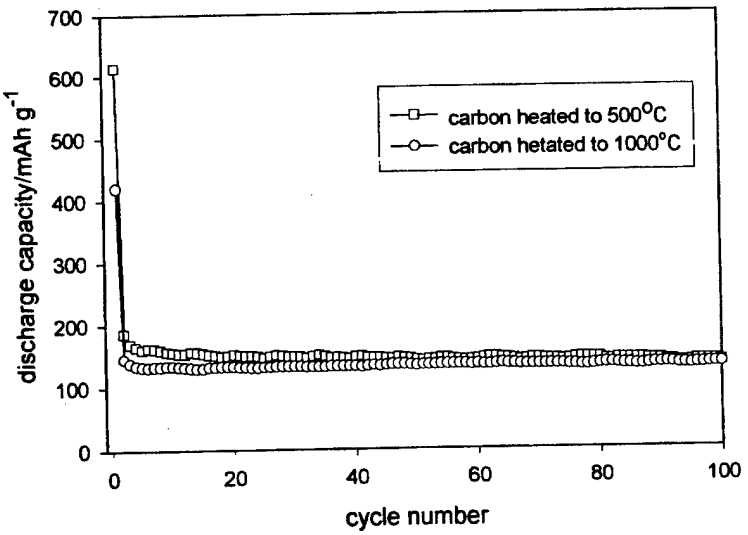


Figure 16. Specific capacity of Li/Carbon cells as a function of cycle number. Carbon was prepared from polyphenol precursor.

3.0 Conclusions

The timeframe allotted for Phase I is nearly complete, predicating an examination of our accomplishment of the proposal initiatives. Our proposal outlined three tasks, (1) Polymer Synthesis, (2) Electrochemical Characterization, and (3) 100 mAh Cell Demonstrations. Task (1) has proved to be a significantly more time-consuming problem

than originally envisioned. However, we believe that we can point to tangible progress in its resolution. The progress of this Phase I can be summarized as follows:

- We have developed, after initial difficulties, a reproducible method of functionalizing target monomers via the Mitsunobu reagent, and subsequently polymerizing the modified monomers utilizing enzyme catalytic methods.[11, 12, 13]

- We have prepared two novel compounds incorporating the structural features believed crucial to enhancing ionic conductivity[14].

- Conductivity measurements have begun on one functionalized polymer and will begin on the second polymer in the closing weeks of Phase I.

- Characterization of all compounds has been completed by high field NMR. High Resolution Electrospray Mass Spectrometry has been carried out on three compounds, several more are scheduled in the next three weeks.

- Type 1 and Type 2 alcohols have been employed in numerous synthetic attempts, despite the lack of commercial availability of requisite starting material (which had been commercially available prior to the submission of the proposal) for the Type 2 analog.

- Establish the techniques to process three type of polymer membranes.

- Conductivities of polyphenol-derived polymers are compatible to pure PEO.

- Polyphenol-derived polymers are not electronic conducting polymers.

- Polyphenol-derived polymers are stable up to 5V vs. Li.

- Promising results in carbonization experiments with ECP-polymers may reveal an important new application for these materials.

The conclusion that may be reached as a consequence of these accomplishments is that the feasibility of the initial plan is supported, and we believe that an expanded series of compounds can be generated with the knowledge we have acquired in this work. All current indications further support the potential utility of these compounds in the proposed battery applications.

4.0 Future Work

- Synthesize ECP-polyphenol derivative materials via the functionalizing phenol-monomer following the enzyme-catalyzed polymerization.

- Scale up the material synthesis.
- Increase the polymer conductivities using composite electrolyte approach through the addition of nanosacle inert powers.
- Incorporate polymer materials in the composite electrodes and use as a separator for cell testing.

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