

# Polymer electrolytes based on polymers derived from phosphazenes

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Recent developments in the area of phosphazene based polymer electrolytes are summarized. The types of polymers utilized, their synthesis and the ion transport studies carried out on the derived polymer electrolytes are highlighted.

THE phenomenon of ionic conductivity is commonly associated with liquids. However, as early as in 1834 Faraday demonstrated that  $\text{PbF}_2$  is highly conducting. It has been later shown that the conductivity in this substance arises not due to electrons but because of fluoride ions which diffuse rapidly through the  $\text{PbF}_2$  structure. In another early experiment, Tubandt showed that the conductivity of  $\text{AgI}$  above  $150^\circ\text{C}$  is due to the motion of  $\text{Ag}^+$  ions<sup>1</sup>. Subsequent research has shown a number of examples of solids that can function as electrolytes. These materials which show appreciable ionic conductivity in the range of  $10^{-6} \leq \sigma \leq 10^{-1} \text{ S cm}^{-1}$  have come to be known as *Solid Ion Conductors*, *Solid Electrolytes* or *Fast Ion Conductors*<sup>2-4</sup>. The types of solids that show the conductivity properties include ceramics such as  $\beta$ -alumina  $[(\text{Na}_2\text{O})_x \cdot 11\text{Al}_2\text{O}_3]$ , NASICON  $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$  (which transport  $\text{Na}^+$ ), zirconia modified with doping  $\text{Ca}^{2+}$  or  $\text{Y}^{3+}$  (oxide ion conductors) or even soft covalent materials such as  $\text{AgI}$  (transports  $\text{Ag}^+$ ). The interest in these kinds of materials stems from the potential they have in several electrochemical applications such as high energy density batteries, gas sensors, electrochemical display devices, etc.  $\beta$ -Alumina has already been used as an electrolyte for a sodium-sulfur battery<sup>5</sup>. In a typical cell assembly polycrystalline  $\beta$ -alumina acting as a solid electrolyte is used to separate the molten sodium and sulfur electrodes. Since sodium and sulfur have low equivalent weights and because of the design aspects the battery constructed from these components can store several times more energy per weight and volume in comparison with the conventional lead-acid battery<sup>1,5</sup>.

Despite the advantages that the solid ion conductors seem to possess they also have some drawback because of their solid state nature. Unlike the liquid electrolytes

which are always in contact with the electrodes irrespective of the physical changes to the electrode surface, solid electrolytes can lose contact with electrodes if the latter undergo dimensional changes during the electrochemical reactions. Precisely for this reason the operating temperature of the sodium-sulfur battery is kept at  $300$  to  $350^\circ\text{C}$  which is well above the melting temperature of the electrodes so that they are molten and can remain in contact with the ceramic  $\beta$ -alumina solid electrolyte<sup>1</sup>.

There has been a search for a new class of solid electrolytes based on polymeric materials as the use of the latter can obviate some of the disadvantages of conventional solid electrolytes. If polymers containing glass transition temperatures well below room temperature are used, these can be flexible at ambient temperatures and can be cast into thin films, which would minimize electrical resistance. Also since they can be used as thin films which can adhere to the electrode surface the dimensional changes that electrodes undergo during the electrochemical reactions need not result in a loss of contact between the electrode and the electrolyte<sup>6-12</sup>.

Wright<sup>13-15</sup> and Armand<sup>16-18</sup> through their insight and pioneering work have shown that poly(ethyleneoxide) (PEO)  $(\text{CH}_2\text{CH}_2\text{O})_n$  can solvate a large number of cations and can form stable complexes with them. These polymer-salt complexes have been shown to possess reasonable ionic conductivities. The work of Wright and Armand has stimulated new thinking and today several polymer electrolytes based on carbon and non-carbon backbones are known. Although the polymer most studied continues to be PEO and its modifications<sup>6,7</sup>, several novel polymers have also been utilized for the purpose of designing new polymer electrolytes. Some of these are poly(propyleneoxide), poly(ethyleneglycol), poly(siloxanes), poly(phosphazenes), poly(vinylpyrrolidone), poly(acrylates), poly(ethylenesuccinate), poly(vinylalcohol), poly(ethyleneimine), poly(alkylenesulphides) and so on<sup>6</sup>. Other types of polymeric systems studied include polymers with network structures<sup>19,20</sup> and 'gel' polymer electrolytes which are prepared by the incorporation of liquid electrolytes into a polymer matrix such as poly(acrylonitrile)<sup>21</sup> or poly(vinylchloride)<sup>22</sup>. An approach termed as 'polymer-in-salt' electrolytes where a small amount of polymer is

This paper is dedicated to Prof. S. S. Krishnamurthy on his 60th birthday.

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combined with salt mixtures has also been employed<sup>23</sup>. In this article we describe polymeric systems based on phosphazenes that have been utilized for the preparation of polymer electrolytes. These include two types of polymeric frameworks. The first class of these polymers are polyphosphazenes which contain a back-bone comprised of alternating phosphorus and nitrogen atoms and where the phosphorus atom bears two exochain substituents. In these polymers the co-ordinating properties are imparted to the macromolecule by the choice of appropriate substituents on the phosphorus atom. The second type of polymers are made up of a carbon back-bone appended to which are cyclophosphazene pendant groups. The cyclophosphazene pendant groups now bear the appropriate substituents required for coordinating to alkali metal ions (Chart 1).

### Poly(phosphazenes) containing organic substituents on phosphorus

Among the various polymers that have been studied for the purpose of forming polymer electrolytes polyphos-

phazenes are among the recent examples<sup>6,7</sup>. In order to select a polymer for the purpose of studying it for a polymer electrolyte several requirements have to be fulfilled<sup>12</sup>. Briefly, the polymer should contain coordinating units either on the backbone or in the side chain. These are usually nitrogen or oxygen atoms. Usually the design of polymers for the preparation of polymer electrolytes containing alkali metal ions such as lithium ion requires the presence of oxygen atoms in the polymer. In PEO the backbone oxygen atoms serve to function as the coordinating atoms. In polyphosphazenes the oligoethoxy substituents on the phosphorus atoms provide the necessary coordination environment. A second important criterion is that the polymer has to be amorphous and should have a low glass transition temperature<sup>12</sup>. Studies by Berthier *et al.* have shown that the large segmental motions that occur above the  $T_g$ 's in amorphous polymers are largely responsible for the ionic conductivity seen in the polymer-salt complexes derived from these systems<sup>24</sup>.

Polyphosphazenes are derived from the parent polymer poly(dichlorophosphazene)  $[\text{NPCl}_2]_n$  **1a** which is prepared by a ring-opening polymerization of the six-membered ring  $\text{N}_3\text{P}_3\text{Cl}_6$  **1**. Macromolecular substitution on **1a** by a variety of nucleophiles can afford polyphosphazenes containing different substituents<sup>25,26</sup>. The torsional freedom in **1a** is considerable and arises from two key structural features. One, unlike normal organic polymers, in **1a** (and in polymers derived from **1a**) the exochain substituents are present only on the alternating atom of the backbone. Thus only the phosphorus atom of the polymer bears two substituents while the nitrogen atom has none. This feature is also present in the isoelectronic polysiloxanes where the silicon atom has the substituents while oxygen atom has none. Secondly since phosphorus can use any of the 3d orbitals for multiple bonding, a torsion of a P-N bond can bring the nitrogen *p*-orbital into an overlapping position with a *d*-orbital at almost any torsion angle. It has been suggested that due to these two structural features the inherent torsional barrier for the backbone bonds may be quite low (0.1 kcal per bond)<sup>26</sup>. Thus many polyphosphazenes containing small or flexible substituents have quite low  $T_g$ 's, making them suitable candidates for trying in polymer-salt complexes.

### Methoxy ethoxy ethoxy polyphosphazene (MEEP) and its modifications

The first example of a polyphosphazene that has been tried for the preparation of polymer-salt complexes is MEEP<sup>27</sup> which is an oligoethoxy side chain containing polymer prepared as shown in Scheme 1. It is to be noted that the polymer is soluble in water and therefore separation of the polymer from the sodium chloride

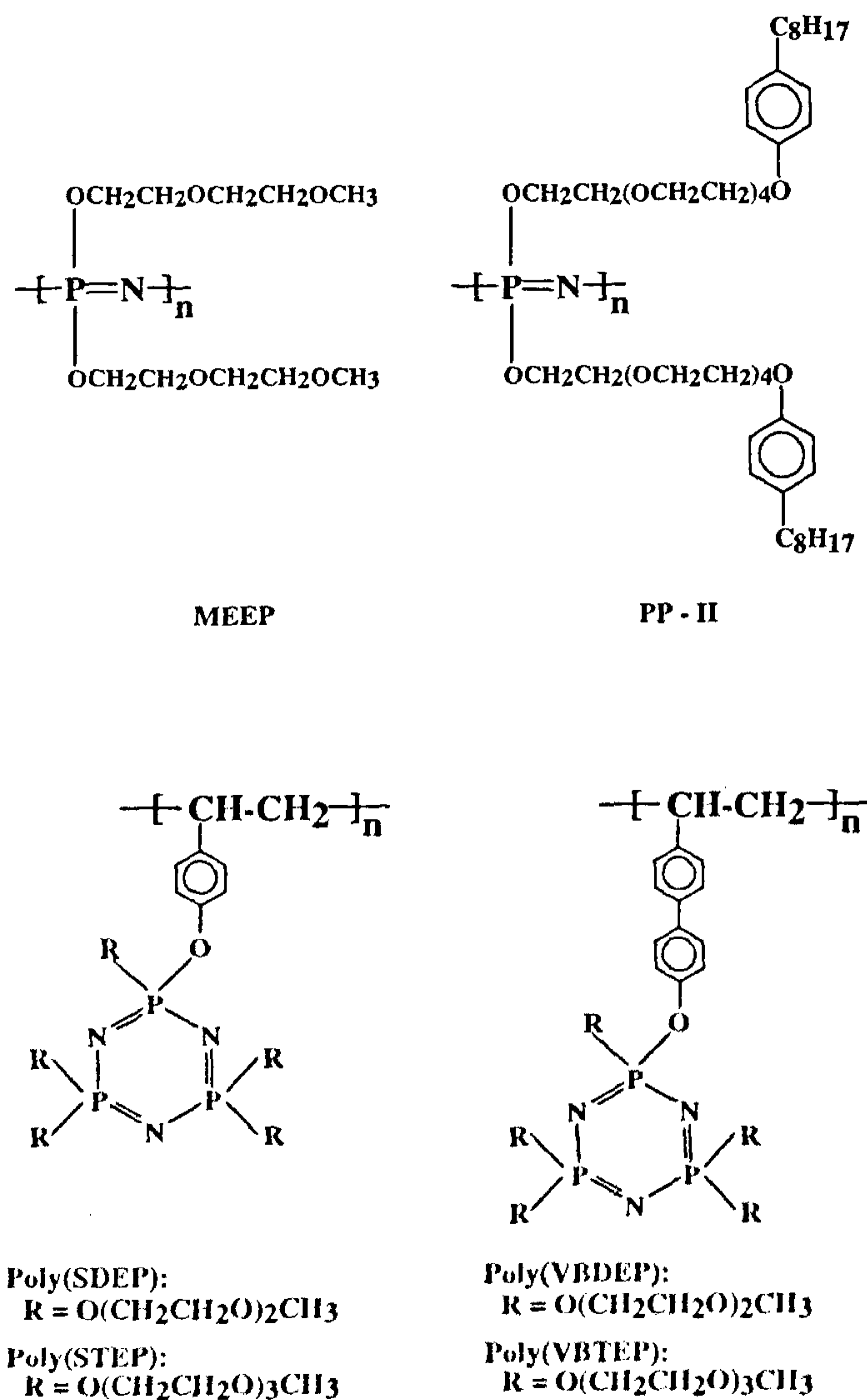
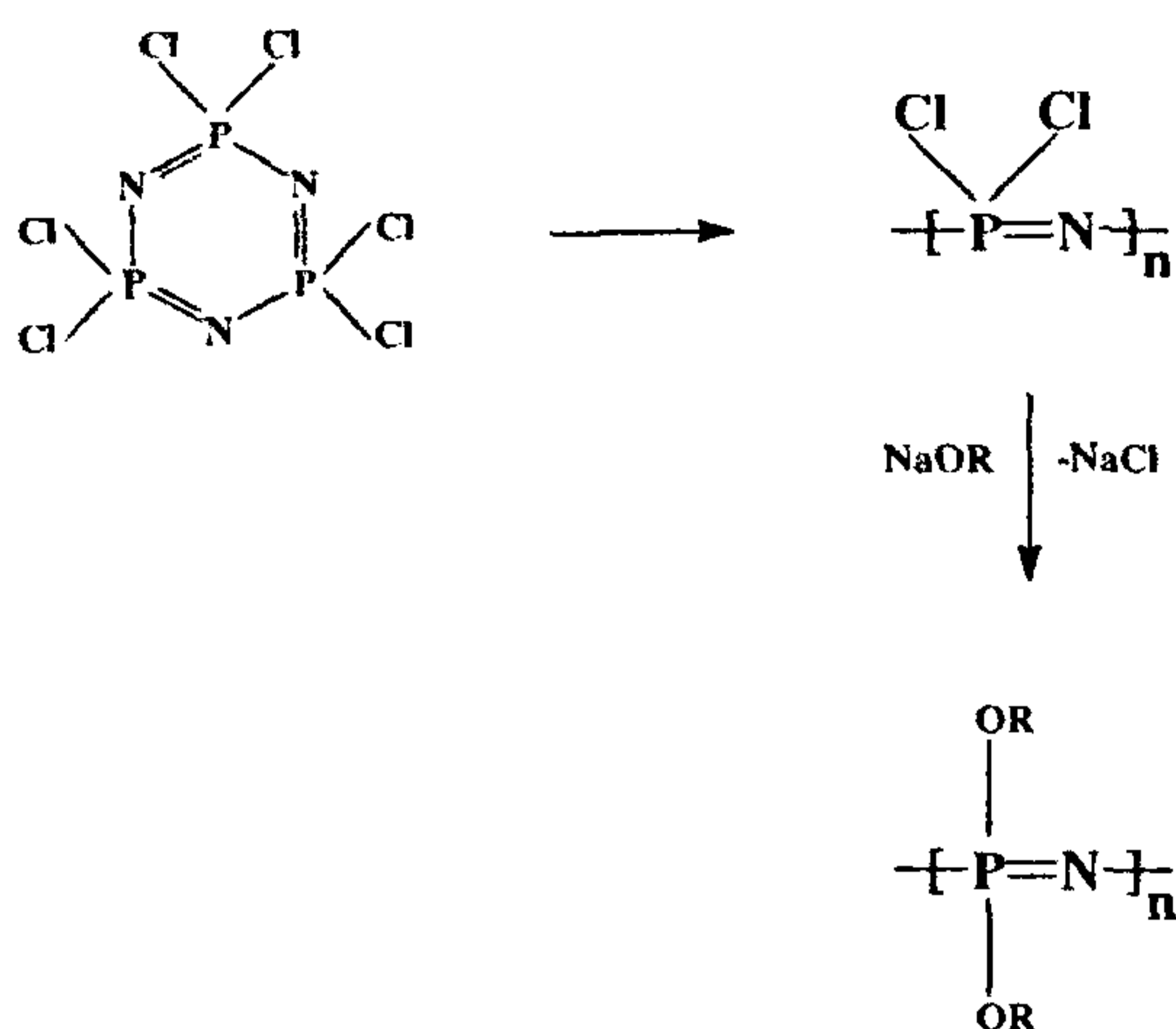


Chart 1.



MEEP, R =  $-\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$

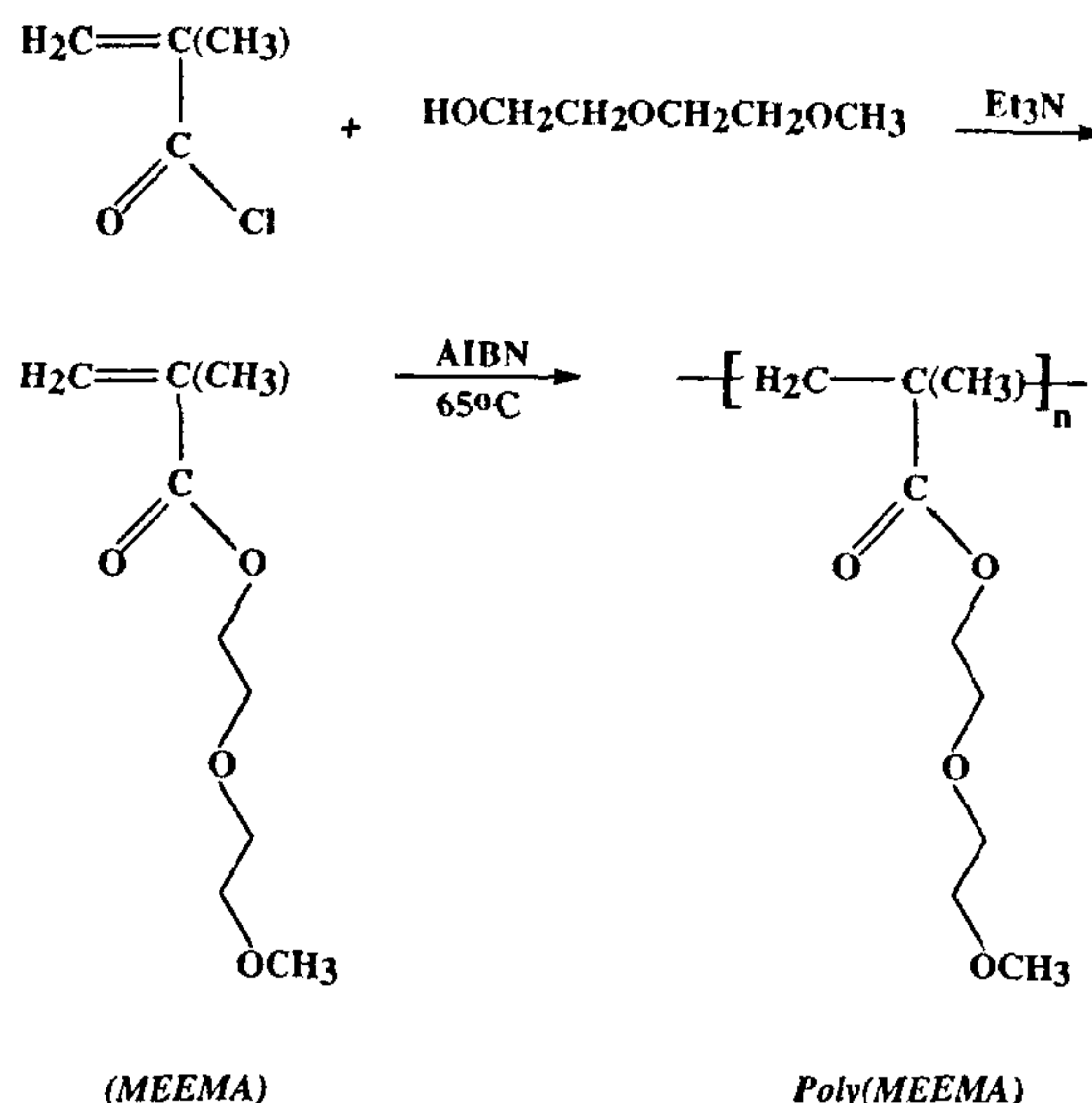
PP(I), R =  $-\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-\text{C}_6\text{H}_4-\text{C}_8\text{H}_{17}$

PP(II), R =  $-\text{OCH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_4\text{O}-\text{C}_6\text{H}_4-\text{C}_8\text{H}_{17}$

Scheme 1.

formed in the reaction involves lengthy dialysis procedures. MEEP is a completely amorphous polymer with a  $T_g$  of  $-83.5^\circ\text{C}$ . It forms complexes with a large number of metal salts<sup>27</sup>. The glass transition temperatures of the polymer-salt complexes increase with an increase of salt concentration. The ionic conductivity also initially increases as the salt concentration increases; however after reaching an optimum value it starts to drop. Some of the conductivity data obtained for MEEP and related systems (*vide infra*) are summarized in Table 1. A high conductivity of  $5.2 \times 10^{-5} \text{ S cm}^{-1}$  is obtained for the MEEP- $\text{LiBF}_4$  complex at an O:Li ratio of 36:1 at room temperature. Although the conductivity of MEEP-metal salt complexes is reasonable the materials are not dimensionally stable and have unfavourable creep properties and therefore cannot be used in devices. Several approaches have been used to overcome this problem<sup>6,7</sup>. Analogues of MEEP with a sulphur atom in the side chain  $[\text{NP}(\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SCH}_3)_2]_n$ , have also been recently prepared<sup>28</sup>.

Recently we have prepared a simple organic polymer containing a similar side chain as in MEEP. This polymer is abbreviated as poly(MEEMA)<sup>29-32</sup>. The polymer is synthesized according to the methodology shown in Scheme 2. Poly(MEEMA) is an amorphous polymer with a  $T_g$  of  $-26.5^\circ\text{C}$ . This polymer forms metal complexes with several lithium salts and seems to coordinate to the lithium ions with the etheroxy oxygen atoms along with the carbonyl oxygen. The measurement of conduc-



Scheme 2.

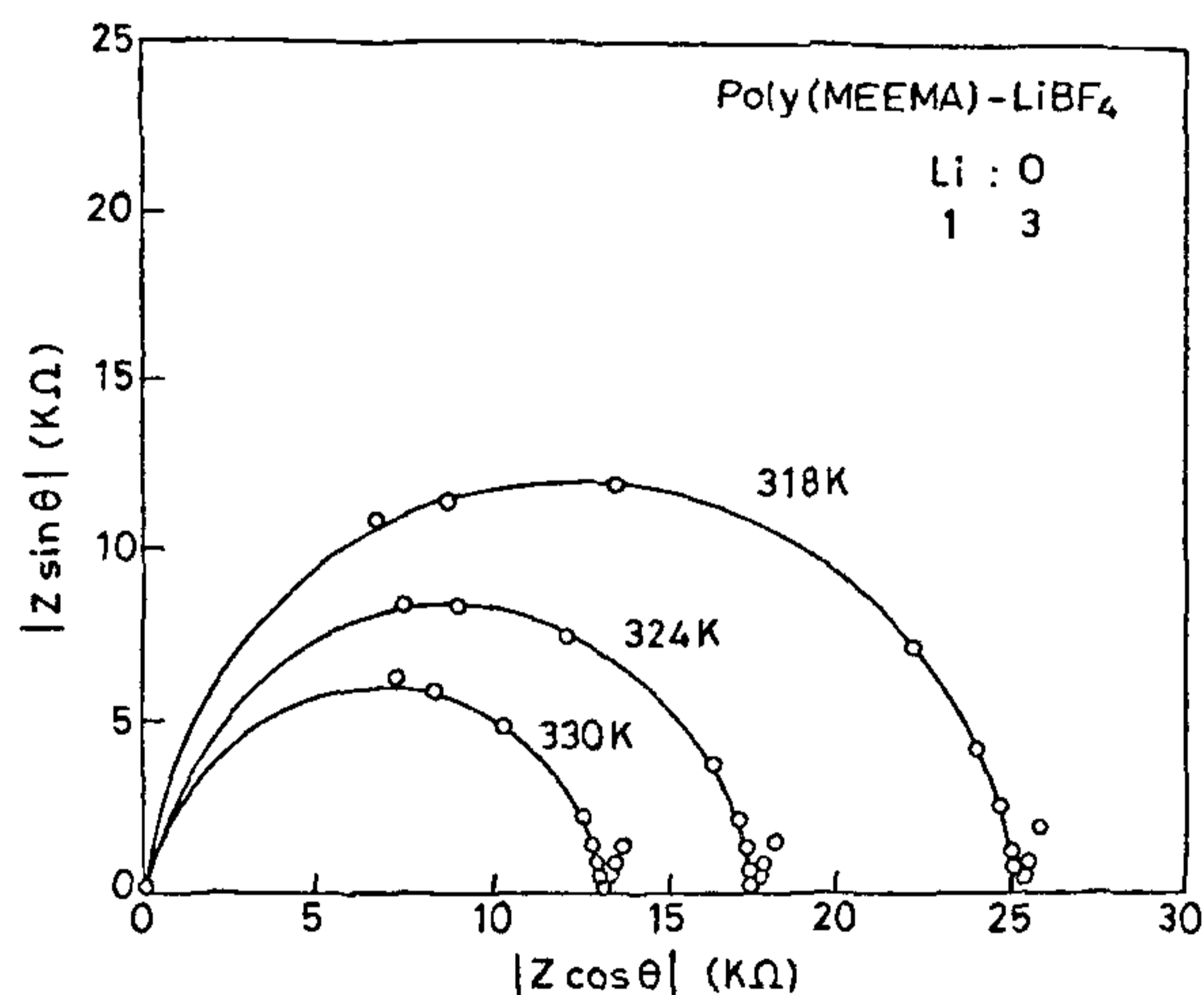


Figure 1. Impedance spectra for poly(MEEMA)- $\text{LiBF}_4$  polymer electrolytes (O:Li ratio 3:1) at three different temperatures. (Taken from ref. 30.)

tivity carried out on these electrolytes has been accomplished by the ac impedance spectroscopy<sup>6,12</sup>. A typical impedance spectrum of the poly(MEEMA)- $\text{LiBF}_4$  complex is shown in Figure 1. A conductivity plot for this system is shown in Figure 2. It can be seen that while the virgin polymer is an insulator the polymer metal salt complexes show significant ionic conductivity with the highest value being obtained for the complex with  $\text{LiBF}_4$ . The conductivity increases with added salt concentration and reaches an optimum value beyond which the addition of salt has a detrimental effect on their conductivity. This is believed to be due to three

**Table 1.** Conductivity values of some polymer electrolytes derived from MEEP and modified MEEP

Polymer	Metal salt	O:Li ratio	Conductivity S cm <sup>-1</sup>	Ref.	
[NP(OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> ) <sub>2</sub> ] <sub>n</sub> , MEEP	—	—	8.1 × 10 <sup>-8</sup> (303); 2.1 × 10 <sup>-7</sup> (363)	6	
	AgCF <sub>3</sub> SO <sub>3</sub>	48:1	2.6 × 10 <sup>-4</sup> (303); 1.4 × 10 <sup>-3</sup> (363)	6	
	LiCF <sub>3</sub> SO <sub>3</sub>	24:1	2.7 × 10 <sup>-5</sup> (303); 2.2 × 10 <sup>-4</sup> (363)	6	
	LiBF <sub>4</sub>	36:1	5.2 × 10 <sup>-5</sup> (303); 8.7 × 10 <sup>-4</sup> (363)	6	
	LiBr	36:1	8.4 × 10 <sup>-6</sup> (303)	6	
	LiNO <sub>3</sub>	36:1	1.1 × 10 <sup>-5</sup> (303)	6	
[NP((OCH <sub>2</sub> CH <sub>2</sub> ) <sub>x</sub> .OCH <sub>3</sub> )] <sub>n</sub> x = 7, ME7P	LiCF <sub>3</sub> SO <sub>3</sub>	95:1	2.4 × 10 <sup>-5</sup> (303); 1.1 × 10 <sup>-4</sup> (363)	6	
	x = 12, ME12P	LiCF <sub>3</sub> SO <sub>3</sub>	24:1	1.4 × 10 <sup>-5</sup> (303); 1.5 × 10 <sup>-4</sup> (354)	6
	x = 17, ME17P	LiCF <sub>3</sub> SO <sub>3</sub>	222:1	1.2 × 10 <sup>-6</sup> (305); 6.2 × 10 <sup>-5</sup> (343)	6

**Table 2.** Conductivity data of poly(MEEMA)-Li salt complexes

Metal salt	Li/O ratio	σ S cm <sup>-1</sup> (K)	Ref.
LiCF <sub>3</sub> SO <sub>3</sub>	1:20	2.3 × 10 <sup>-6</sup> (270); 6.0 × 10 <sup>-5</sup> (303)	6
LiClO <sub>4</sub>	1:10	3.3 × 10 <sup>-6</sup> (305); 1.0 × 10 <sup>-5</sup> (323)	6
LiBF <sub>4</sub>	1:5	5.8 × 10 <sup>-5</sup> (300); 2.0 × 10 <sup>-4</sup> (318)	6
	1:6	4.0 × 10 <sup>-5</sup> (300)	6

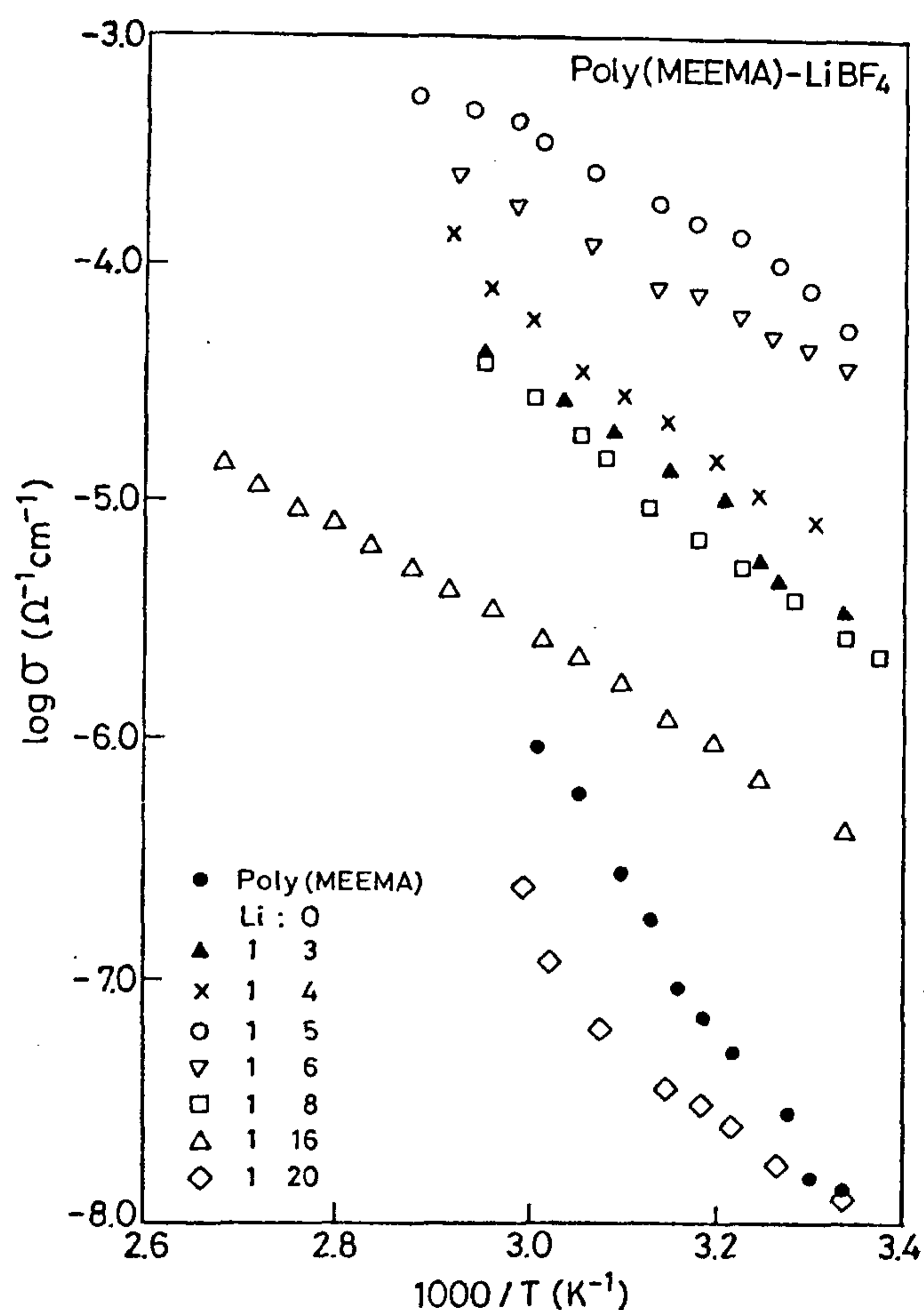
$$\sigma = A \exp(-E_A/kt).$$

Or the VTF (Vogel-Tamann-Fulcher) equation<sup>6</sup>

$$\sigma = AT^{-1/2} \exp[(-B/k(T-T_0))].$$

Most of the conventional solid electrolytes as well as some crystalline polymer electrolytes obey the Arrhenius equation. In contrast, amorphous polymer electrolytes obey the VTF equation<sup>6</sup>. This is illustrated in Figure 3 where a VTF plot for the poly(MEEMA)-LiBF<sub>4</sub> complexes are shown. The activation energies obtained are summarized in Table 3. Figure 4 shows the conductivity isotherm plots. It is clearly seen from the plot that whereas in the poly(MEEMA)-LiClO<sub>4</sub> system an enhancement in conductivity of about 20 times is seen at 328 K in the poly(MEEMA)-LiBF<sub>4</sub> this enhancement is 2240 times at 324 K. The enhancement in conductivity value is with respect to the virgin polymer. An additional feature of this system is that these polymer electrolytes are dimensionally stable unlike the materials obtained from MEEP.

Another approach towards solving the dimensional stability problem of MEEP has been the synthesis of cross-linked versions of MEEP. Both chemical and radiation methods of cross-linking have been tried. Also physical blends of MEEP with various polymers such as PEO, poly(propylene oxide), poly(ethylene glycol diacrylate) and poly(vinyl pyrrolidone) have been prepared. These materials possess better dimensional stability in comparison with MEEP while having comparable conductivity properties for their salt complexes<sup>6</sup> (Table 1).

**Figure 2.** Conductivity plots ( $\log \sigma$  vs  $10^3/T$ ) of poly(MEEMA)-LiBF<sub>4</sub> polymer electrolytes. (Taken from ref. 30.)

reasons. As the salt concentration increases, there is a decrease in the number of coordination sites. Secondly the polymers lose their flexibility owing to ionic cross-linking and lastly salt aggregates and ion-pair formation also increase with increased salt concentration<sup>6,12</sup>. The conductivity for the poly(MEEMA)-LiX system is summarized in Table 2. The ionic conductivity observed in polymer electrolytes can be explained by either the Arrhenius equation

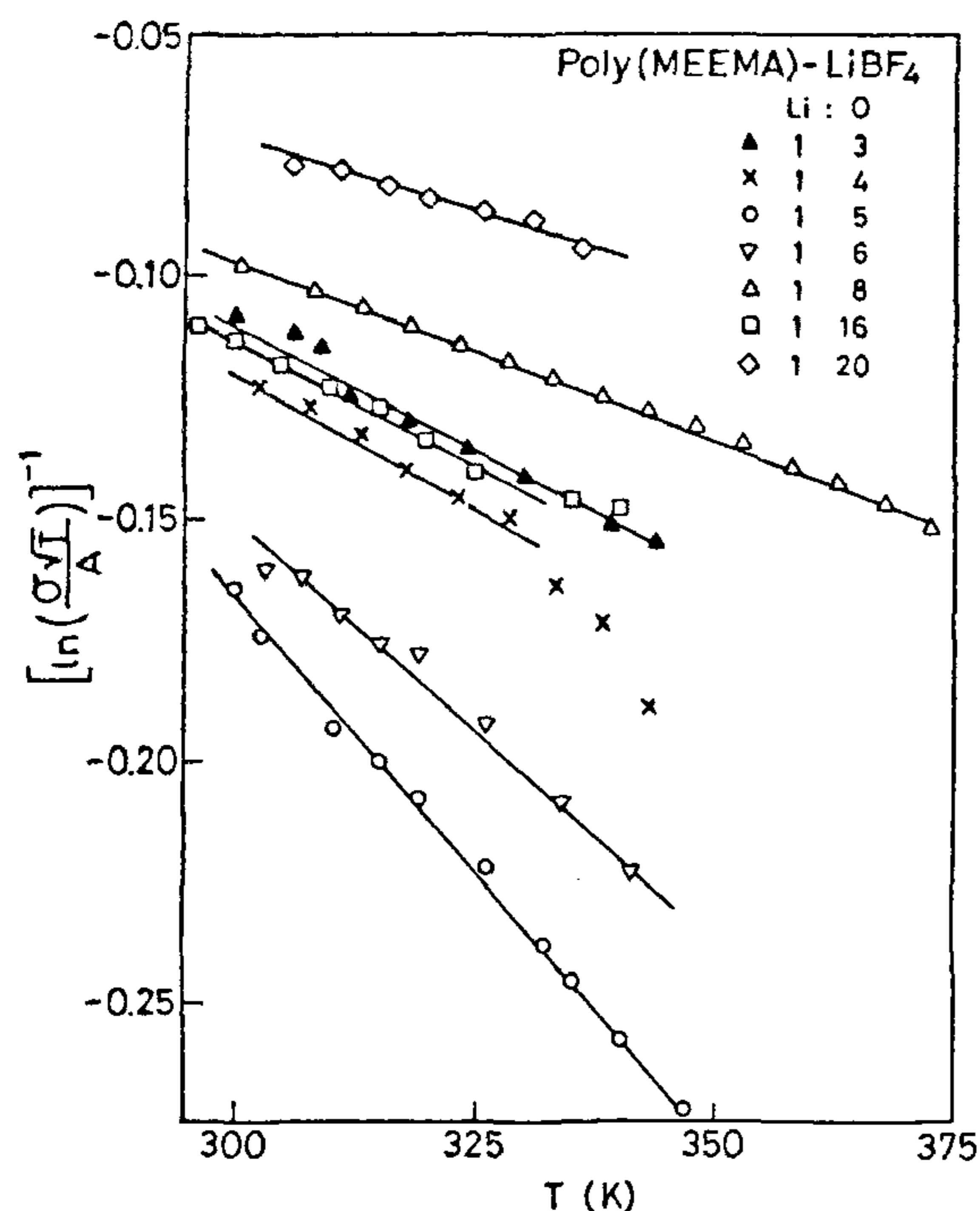


Figure 3. VTF plots for poly(MEEMA)-LiBF<sub>4</sub> complexes. (Taken from ref. 30.)

Table 3. Activation energy parameters obtained for poly-(MEEMA)-Li salt complexes from fitting VTF equation

Composition (Li:O ratio)	A	B (eV)	T (K°)
Poly(MEEMA)-LiClO <sub>4</sub>			
1:8	0.333	$4.24 \times 10^{-2}$	263
1:10	0.286	$8.66 \times 10^{-2}$	187
1:12	0.250	$4.64 \times 10^{-2}$	254
1:20	0.167	$7.38 \times 10^{-2}$	224
1:30	0.118	$1.15 \times 10^{-1}$	196
Poly(MEEMA)-LiBF <sub>4</sub>			
1:3	0.571	$7.69 \times 10^{-2}$	204
1:4	0.500	$5.44 \times 10^{-2}$	229
1:5	0.444	$4.08 \times 10^{-2}$	220
1:6	0.400	$5.19 \times 10^{-2}$	208
1:8	0.333	$9.31 \times 10^{-2}$	177
1:16	0.200	$6.06 \times 10^{-2}$	252

### Surfactant substituted polyphosphazenes

Although the polymer electrolytes prepared from MEEP show good ionic conductivity as described *vide supra* the preparation of MEEP entails cumbersome dialysis procedures to separate the polymer from the sodium chloride which is formed as a side product in the reaction. Further, MEEP is hydrophilic and this is an undesirable feature particularly in the context of applications

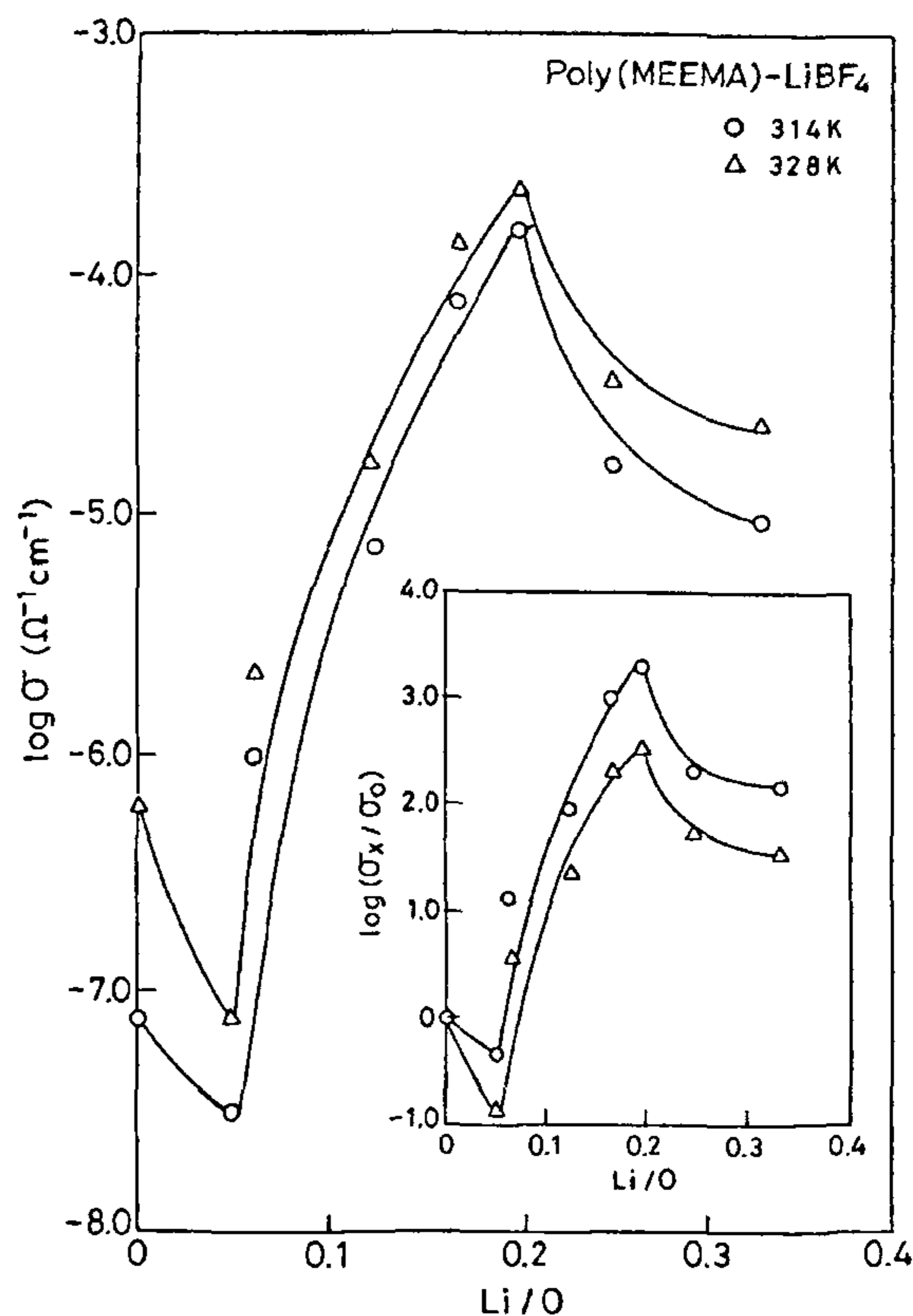


Figure 4. Conductivity isotherm plots at 314 and 328 K for different compositions of poly(MEEMA)-LiBF<sub>4</sub> complexes. Insets are the  $\log(\sigma_x/\sigma_0)$  vs Li/O ratio plots. (Taken from ref. 30.)

Table 4. Properties of polymers PP(I) and PP(II)

Measurement	PP(I)	PP(II)
<sup>31</sup> P NMR (ppm)	-7.42	-7.2
M <sub>w</sub>	$8.7 \times 10^{-5}$	-
$\eta_{\text{intrinsic}}$ (ccg <sup>-1</sup> )	94.11	17.62
TGA	164.8°C (I) 337.6°C (II) 458.0° (III)	289.4°C (I) 361.5°C (II)
DSC (T <sub>g</sub> )	-13.28°C	-28.8°C
XRD	Amorphous	Amorphous
SEM	Amorphous	Amorphous

in devices such as lithium batteries<sup>33</sup>. One of the ways of overcoming this problem is to be able to prepare water insoluble analogues of MEEP. We have recently reacted two commercially available surfactants with the poly(dichlorophosphazene) **1a** to obtain the polymers PP-1 and PP-2 (Scheme 1). Both of these polymers are completely insoluble in water besides being hydrophobic. Also they show remarkable solubility properties being soluble in a wide range of solvents including hexane. These polymers are also amorphous and the T<sub>g</sub>'s of PP-1 and PP-2 are -13.2°C and -28.8°C respec-

**Table 5.** Conductivity values of polymer electrolytes derived from surfactant substituted poly(phosphazenes) PP(I) and PP(II)

Composition O:Li	PP(I) - LiClO <sub>4</sub>			Ref.
	$\sigma$ (S cm <sup>-1</sup> ) 310 K	$\sigma$ (S cm <sup>-1</sup> ) 333 K	$\sigma$ (S cm <sup>-1</sup> ) 333 K	
6:1	$4.0 \times 10^{-8}$	$4.4 \times 10^{-7}$	$1.0 \times 10^{-6}$	6
12:1	$2.4 \times 10^{-8}$	$8.7 \times 10^{-8}$	$1.3 \times 10^{-7}$	6
18:1	$1.9 \times 10^{-8}$	$2.6 \times 10^{-8}$	$4.2 \times 10^{-8}$	6
Composition O:Li	P(II) - LiBF <sub>4</sub>			Ref.
	$\sigma$ (S cm <sup>-1</sup> ) 303 K	$\sigma$ (S cm <sup>-1</sup> ) 333 K	-	
5:1	$7.6 \times 10^{-7}$	$1.3 \times 10^{-6}$	-	6
8:1	$2.3 \times 10^{-7}$	$5.8 \times 10^{-6}$	-	6
12:1	$6.9 \times 10^{-8}$	$2.5 \times 10^{-6}$	-	6

**Table 6.** Activation energies obtained for PP(II)-LiBF<sub>4</sub> from fitting the Arrhenius equation

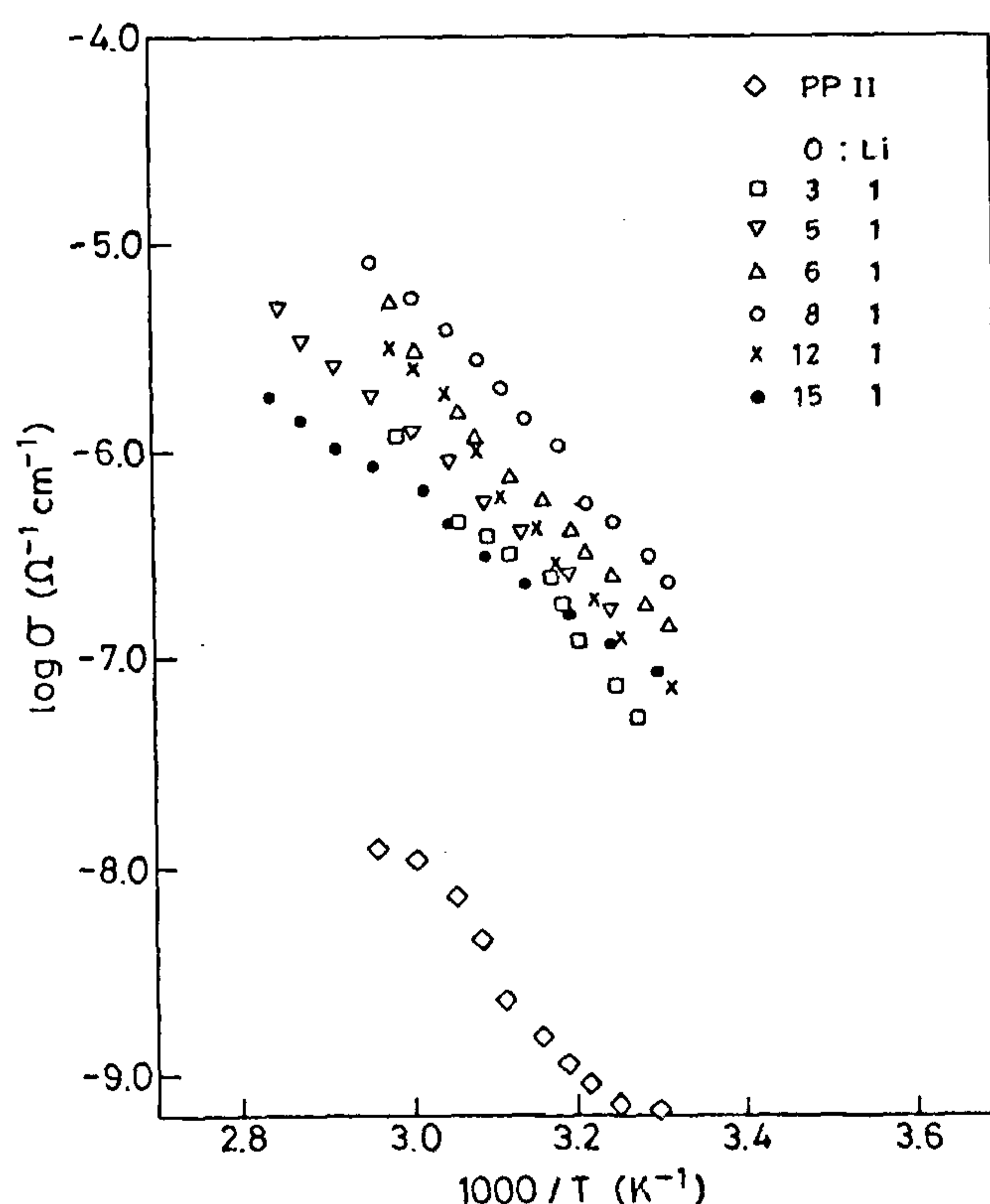
O:Li	Activation energy (eV)	A
3:1	0.47	0.800
5:1	0.65	0.674
6:1	0.84	0.666
8:1	0.69	0.600
12:1	0.63	0.500
15:1	0.49	0.444

tively<sup>34,35</sup>. The properties of these polymers are summarized in Table 4. Both of these polymers form lithium salt complexes. The conductivity studies reveal that while the conductivities observed for the polymer metal salt complexes involving the shorter etheroxy side chains (PP-1) are not significant, those observed with PP-2 are very good. The conductivity plot of PP(II)-LiBF<sub>4</sub> complexes along with a plot of  $\log \sigma$  vs Li/O ratios for the same system are shown in Figures 4 and 5. The conductivity data observed for this system are summarized in Table 5. Unlike the polymer electrolytes obtained from poly(MEEMA) or MEEP the conductivity behaviour in these polymer electrolytes is explained by the Arrhenius behaviour<sup>34,35</sup>. The activation energies obtained in this system are summarized in Table 6.

### Other polyphosphazenes

Poly(etheroxy phosphazenes), [NP(O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>x</sub>CH<sub>3</sub>)<sub>2</sub>]<sub>n</sub> where  $x = 1, 2, 7, 12$  and  $17$  have been investigated in terms of the change of chain length on the observed conductivity in the lithium salt complexes of these polymers<sup>6</sup>. With lithium trifluoromethane sulfonate a maximum conductivity of  $2.4 \times 10^{-5}$  S cm<sup>-1</sup> is observed at 30°C when the chain length  $x$  equals seven (Table 1). The conductivity increases to nearly  $1.1 \times 10^{-4}$  S cm<sup>-1</sup> at 90°C.

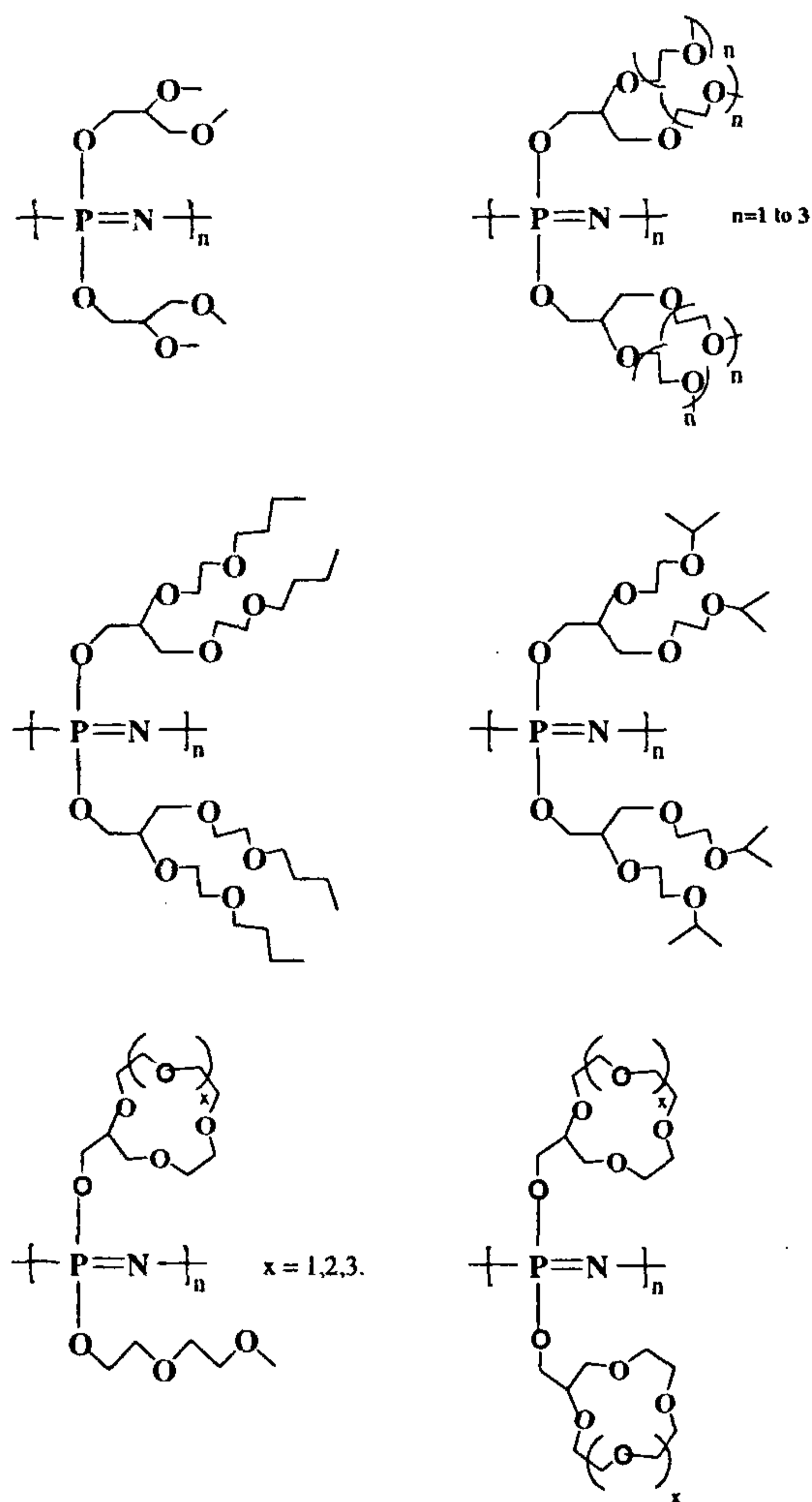
Mixed substituent polyphosphazenes [NP(OR)(OR')]<sub>n</sub> where  $R = \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$  and  $R' = (\text{CH}_2)_n\text{CH}_3$

**Figure 5.** The conductivity plot ( $\log \sigma$  vs  $10^3/T$ ) of PP(II)-LiBF<sub>4</sub> complexes of different O:Li ratios. (Taken from ref. 34)

( $n = 2$  to  $9$ ) have also been investigated with the particular aim to test the effect of free volume *vis-à-vis* the number of coordination sites on ionic conductivity. The maximum conductivity for each polymeric system decreased with an increase in chain length of the alkoxy group<sup>36,37</sup>. Thus although the free volume of the polymer increases with an increase in chain length it also causes a concomitant decrease in the number of coordination sites *per unit volume* of the polymer. This latter feature overrides the free volume and leads to lower ionic conductivities.

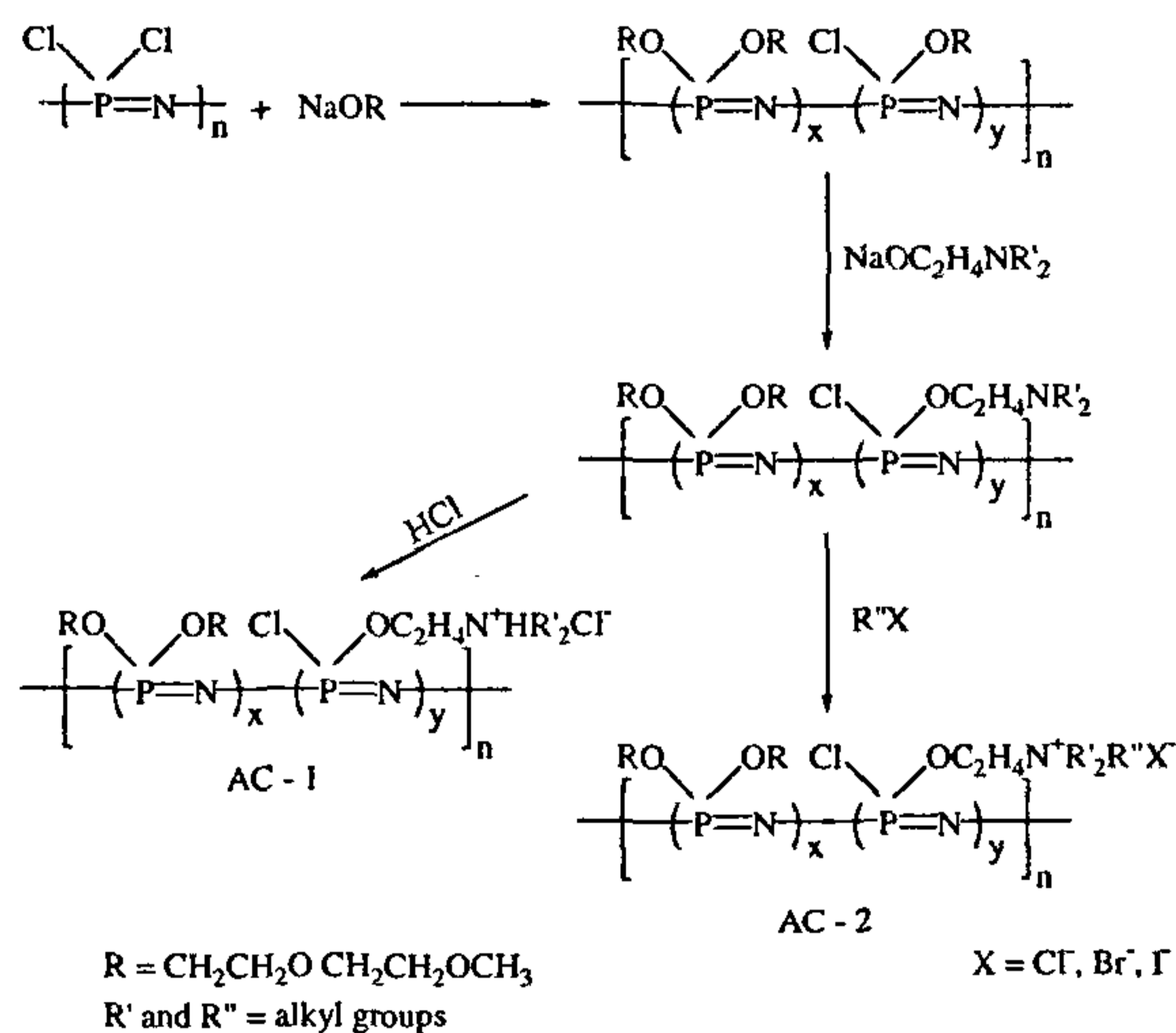
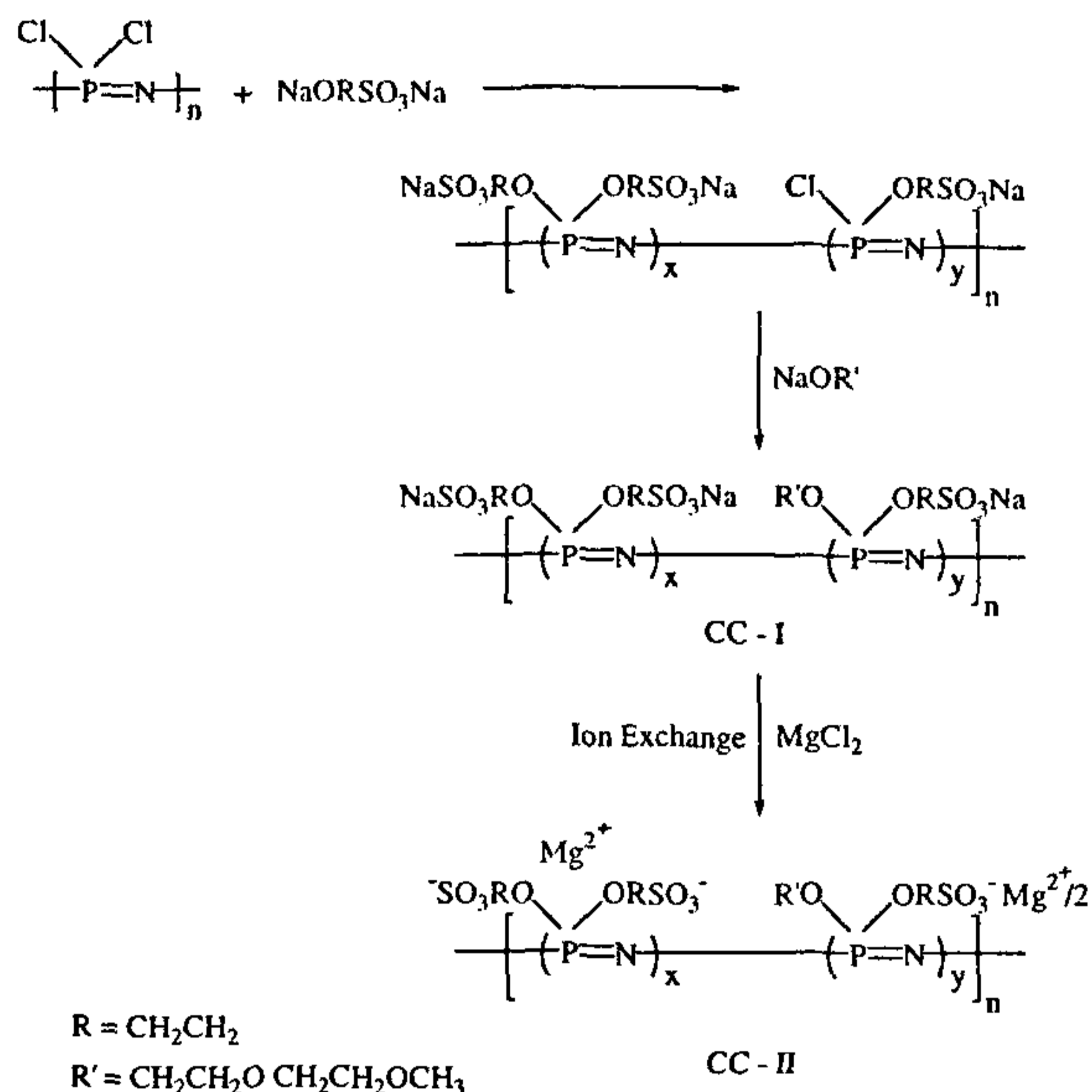
Recently, Allcock and co-workers have synthesized crown-ether linked polyphosphazenes and mixed sub-

stituent polyphosphazenes containing a crown-ether substituent and an ethoxy substituent. The polymers containing only crown ether substituents formed very stable complexes with  $\text{Li}^+$  and therefore showed poor ionic conductivity<sup>38</sup>. Other modifications of MEEP have also been recently synthesized (Chart 2).



### Ionic polyphosphazenes

It was reasoned by Shriver and co-workers that if polymers containing immobilized ionic groups are prepared, their counterions would in principle be able to contribute maximally to the conductivity in a uni-polar conduction mechanism. With this objective polymers CC-I, CC-II, AC-I and AC-II were prepared (Schemes 3 and 4) (refs 39-41). The synthesis of the polymers involved



a sequential replacement of the chlorine atoms by appropriate substituents. Thus the synthesis of CC-I entailed the reaction of the polydichlorophosphazene with  $\text{NaORSO}_3\text{Na}$ . The  $\text{RONa}$  end of the reagent reacts with the  $\text{P-Cl}$  bond to form the  $\text{P-ORSO}_3\text{Na}$  linkage. In this assembly the anionic part, viz.  $\text{SO}_3^-$  is bound to the polymer and therefore is virtually immobile. The sodium cations in contrast are in principle mobile. These polymers would be expected therefore to be essentially cation conductors. Another interesting feature is that the sodium ions can be exchanged by other cations also including divalent cations such as magnesium ions. The

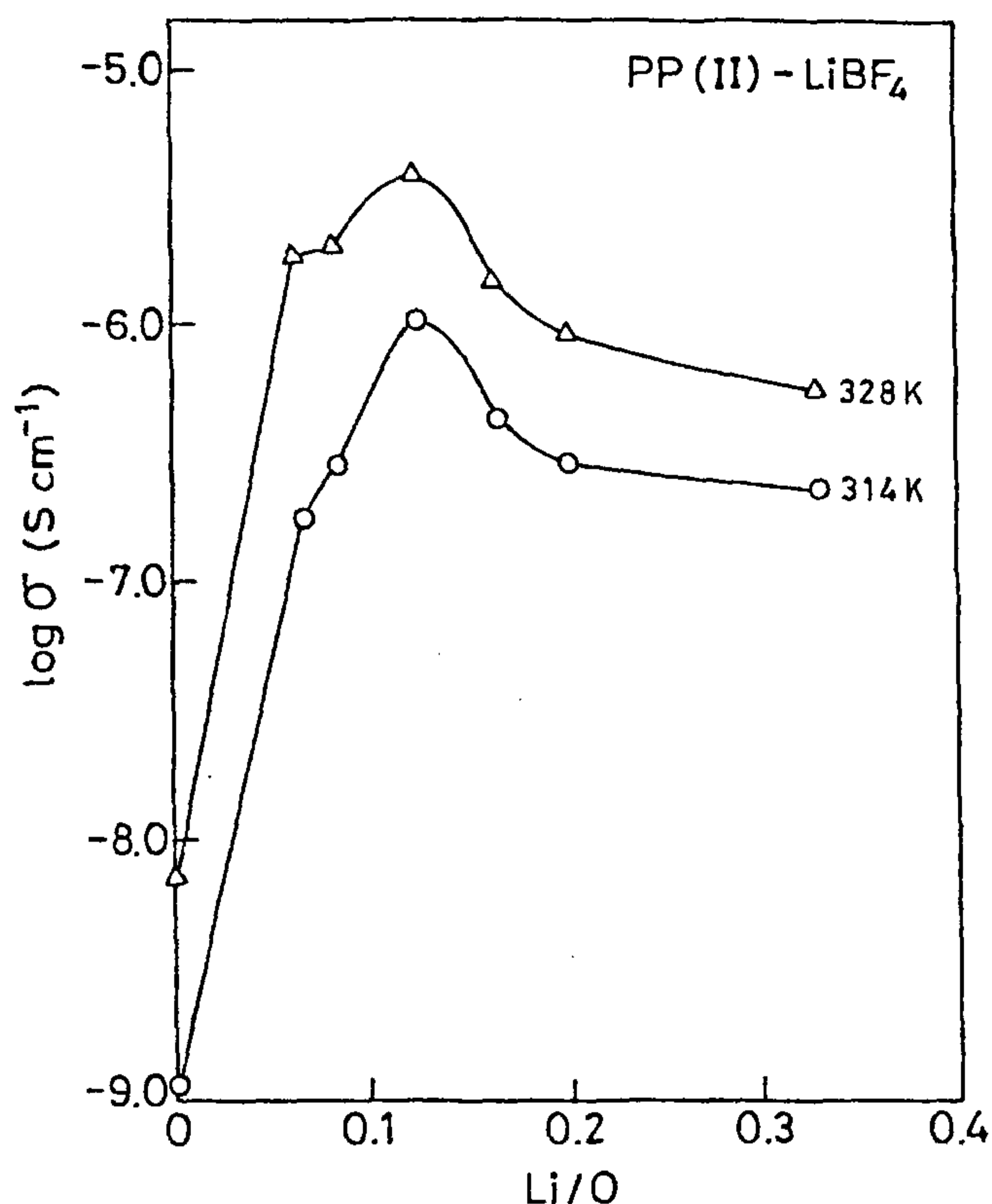
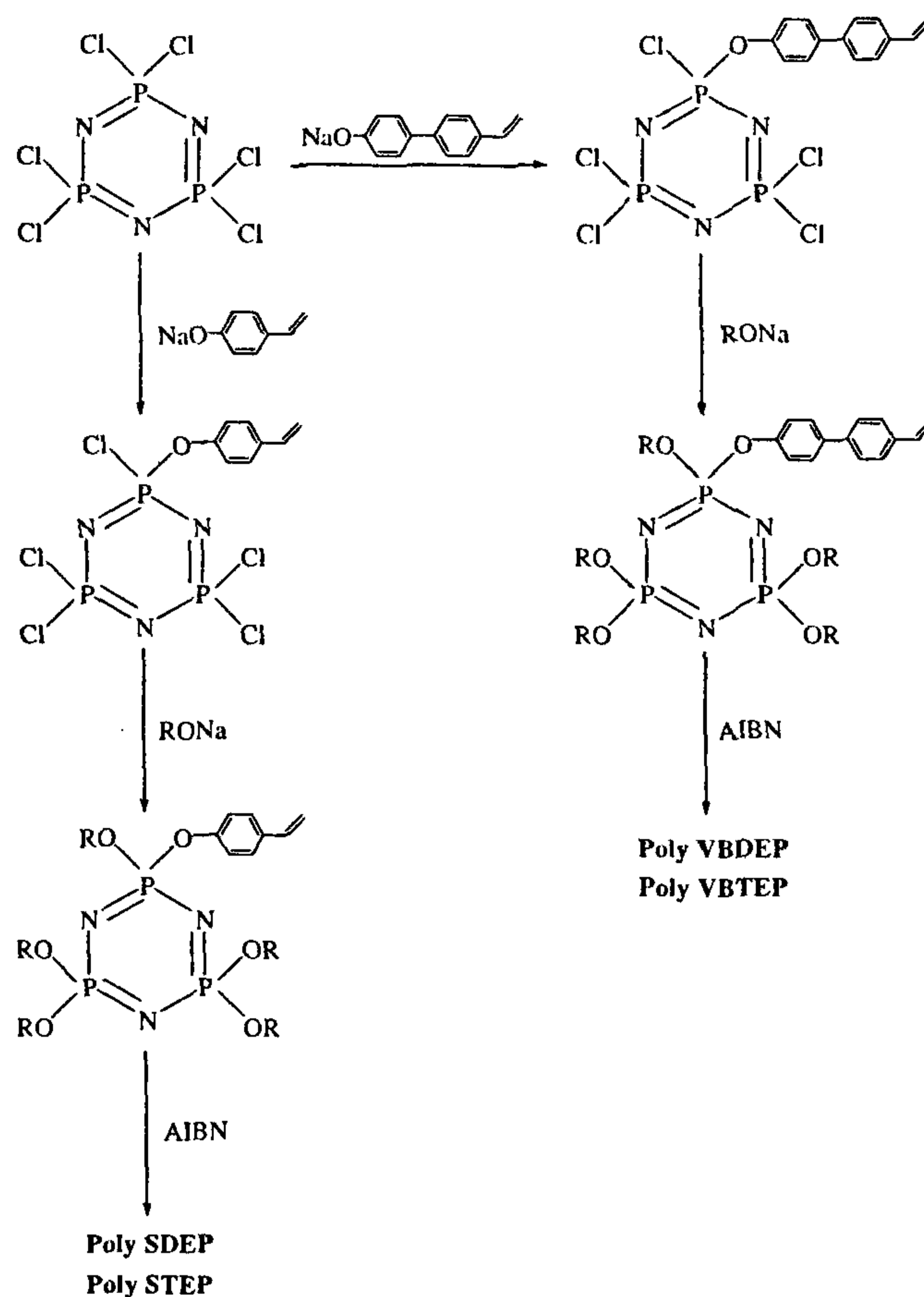


Figure 6. Plot of  $\log \sigma$  vs Li/O ratios for PP(II)-LiBF<sub>4</sub> complexes at 314 and 328 K. (Taken from ref. 34.)

synthesis of the anionic conductors is carried out by the use of a different synthetic strategy. In this methodology part of the chlorine atoms on the polyphosphazene skeleton have been substituted by a tertiary nitrogen containing substituent. The tertiary nitrogen can be subsequently quaternized either by HCl or by an alkyl halide. In this strategy the quaternized cationic fragment is rendered immobile by being anchored to the polymer while the anions are free for the purpose of conduction (Scheme 4). In spite of the novelty of these polymers in terms of their design and preparation, their conductivities were poor presumably due to ion pair formations.

### Pendant cyclophosphazene polymers

In addition to polymers containing the P-N backbone, phosphazene-based polymers can also be prepared in another way. This involves the substitution of a polymerizable (usually a vinyl) organic moiety on the cyclophosphazene skeleton. Polymerization of these monomers affords an organic polymer with a carbon backbone containing the cyclophosphazene rings as regular pendant attachments. In these polymers the backbone is expected to be fairly rigid. Thus it is possible to utilize these type of polymers for testing whether the backbone segmental motion of polyphosphazenes is a critical feature for ionic conductivity. Inoue and co-workers from Japan prepared polymers



Scheme 5.

containing a styrene or a vinyl biphenyl-based polymer containing pendant oligoethoxy substituted cyclophosphazenes<sup>42,43</sup> (Scheme 5). In contrast to the polyphosphazenes described *vide supra* in these polymers, the coordinating ethoxy substituents are not directly linked to the backbone atoms. They are attached to the pendant substituents. Another point of contrast is the high density of coordinating units present in these polymers. This is because of the fact that each pendant cyclophosphazene has *five* oligoethoxy substituents. Besides leading to a high free volume this structural feature also enables the polymers to have low  $T_g$ 's. These polymers readily form Li salt complexes which show room temperature ionic conductivity of the order of  $10^{-5}$  S cm<sup>-1</sup>. These results seem to indicate that as long as there is sufficient segmental mobility of the side oligoethoxy chains the lack of high torsional mobility of the backbone need not be a critical factor for achieving high ion transport. The conductivity behaviour of these polymer electrolytes is typical of amorphous polymer electrolytes and can be accounted by the VTF equation.

### Conclusions and outlook

Phosphazene-based polymers have been very successful as hosts for forming polymer-salt complexes which can



function as excellent electrolytes facilitating ion-transport. As discussed above both the skeletal flexibility of the polymer as well as segmental motion of the substituents seem to be critical for determining ionic conductivity. The advantages that polyphosphazenes have is the ability to fine tune the polymer properties by a simple variation of the substituent on the phosphorus. This principle has been very well demonstrated in the examples described *vide supra*. However, in spite of the impressive strides in terms of the achievement of routine ambient temperature ionic conductivities of the order of  $10^{-5}$  to  $10^{-4}$  S cm $^{-1}$  in the polymer electrolytes derived from these systems there is a long way to go before any of these can be put into use in practical devices. One of the problems is to increase the ionic conductivities to around  $10^{-1}$  S cm $^{-1}$  at room temperature. Another important aspect that has to be ensured is the electrochemical and dimensional stability of these materials. Once these problems are addressed and solved, practical applications of polymer electrolytes will emerge leading to a new generation of materials.

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