

Main-Chain Poly(arylene ether) Phosphonium Ionomers

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Poly(arylene ether) main-chain phosphonium ionomers were successfully synthesized and characterized. The reaction scheme involved first preparing the poly(arylene ether phosphine oxide) by a nucleophilic step or condensation polymerization of bisphenolates on activated aryl halides, wherein phenyl phosphine oxide was the activating group. High-molecular-weight, tough, film-forming polymers were produced with glass transition temperatures of 200°C or higher. The resulting materials were successfully reduced using phenylsilane in refluxing chlorobenzene. The derived phosphine or phosphine/phosphine oxide copolymer was reacted with alkyl halides to produce the phosphonium salts. The resulting materials showed enhanced hydrophilicity and in some cases could be successfully dispersed in water. In addition, chromophores such as Methyl Orange and Methyl Red were combined with the backbone ionomer to produce new film-forming, ionically linked species. The materials are of general interest for situations where water-dispersible intermediates, e.g. coatings, fiber sizings etc. are required. The phosphonium salts can be converted back to the phosphine oxide in fairly high yields by simple thermal methods and in quantitative yield by chemical methods (e.g. the Wittig reaction). © 1998 John Wiley & Sons, Ltd.

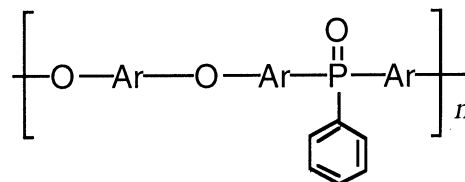
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INTRODUCTION

Ionomers are important polymeric materials containing both covalent and anionic or cationic moieties, and have recently been reviewed.¹ Quaternary onium salts bound to a polymeric system have several industrial applications such as ion-exchange resins and polymer-supported catalysts. Insoluble polystyrene beads or silica gels bearing quaternary ammonium or phosphonium salts, for example, have been synthesized and investigated as high-temperature polymer-supported phase-transfer catalysts in organic synthesis.^{2–5} However, there are many other possible applications for the polymeric onium salts, such as ion-exchange membranes and polymeric ion conductors, which require the polymeric systems to withstand high temperatures for a short period of time during processing or during their long-term application at milder temperatures, but possibly under a corrosive environment.

Poly(arylene ether phosphine oxide)s (**1**; PEPO)s are a relatively new subset of engineering thermo-



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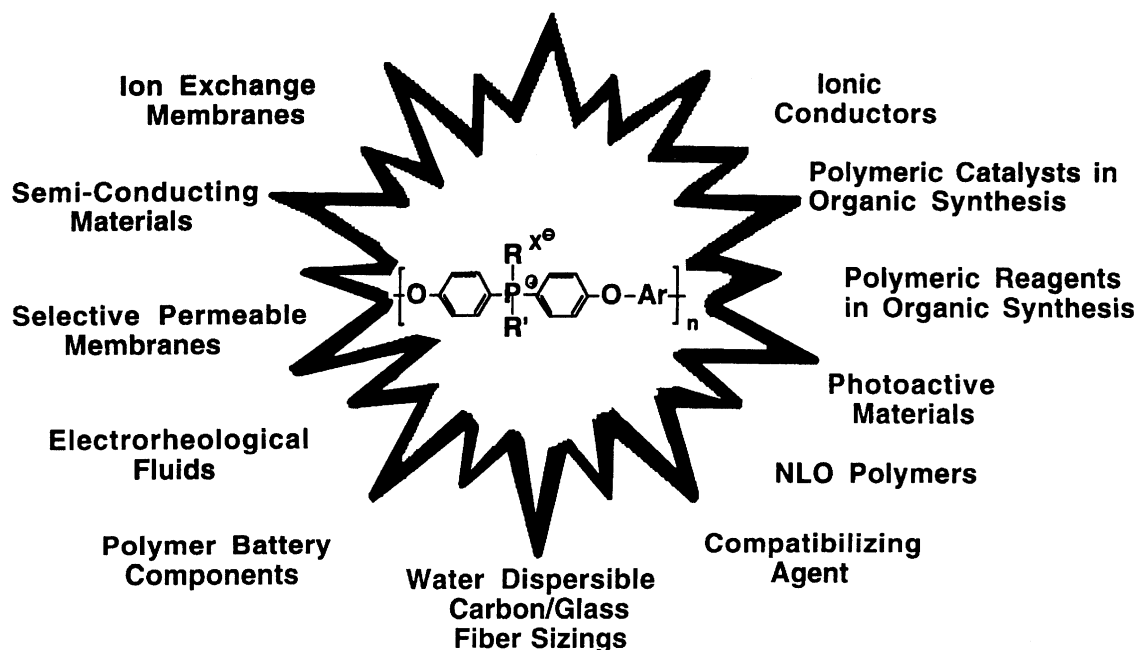


Figure 1 Potential applications for poly(arylene ether phosphonium Salt)s.

plastics which are prepared via nucleophilic aromatic substitution polycondensation of an activated aromatic dihalide and an aromatic bisphenol in the presence of a weak base and an aprotic dipolar solvent.⁶

They show glass transition temperatures in the range of about 200–280 °C. These high-performance thermoplastics have good thermo-oxidative and hydrolytic stability as well as good mechanical properties. Moreover, these phosphorus-containing polymers have been shown to produce fire-resistant materials.⁷

Our research in the past few years has focused on preparation and characterization of several novel phosphorus-containing polymers.^{8–10} Our main goal in preparation of these polymers was, initially, to introduce new matrix systems with superior properties compared with the existing resins, with a special focus on structural adhesives and carbon fiber composites, as well as other possible applications for derivatives such as polymeric phosphines and phosphonium salts.

Previously, the synthesis of poly(arylene ether phosphine)s (PEP)s derived via reduction of PEPOs was reported.⁸ This paper further investigates the reduction of PEPOs to PEPs and the quaternization of PEPs to form a new type of water-dispersible

poly(arylene ether phosphonium salt) (PEPS), which has many potential applications, as shown in Fig. 1.

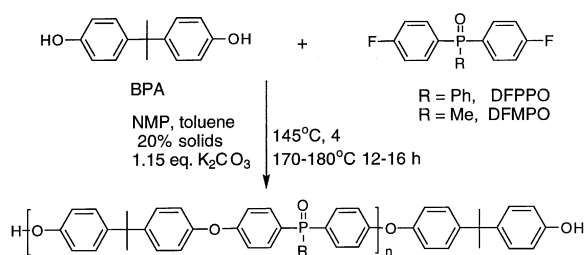
EXPERIMENTAL

General procedures

NMR spectra were recorded using a Varian Unity 400 NMR spectrometer at room temperature. ³¹P NMR chemical shifts are reported relative to 85% H₃PO₄ (external, 0.0 ppm). *N*-Methylpyrrolidinone (NMP), 1,2-dichlorobenzene and chlorobenzene were obtained from Fisher and were vacuum-distilled over calcium hydride and stored under nitrogen before use. All other reagents and solvents were purchased from Aldrich and used as received.

Synthesis of poly(arylene ether phosphine oxide)s (PEPO)s, 1a,b

The preparation of high-molecular-weight PEPOs with general structure **2** is illustrated in Scheme 1. PEPOs **2a** and **2b** were synthesized by reacting bisphenol-A (BPA) with bis(4-fluorophenyl)ph-



Scheme 1 Synthesis of PEPOs **2a** (R = Ph) and **2b** (R = Me).

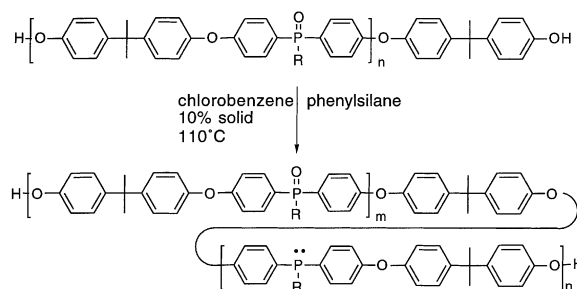
nylphosphine (DFPPO) and bis(4-fluorophenyl)-methylphosphine (DFMPO), respectively, using the same procedure reported previously.⁷⁻¹⁰ The number-average molecular weight of **2a** was 30,000 g/mol⁻¹. The polymers were vacuum dried at 200 °C for 24 h before further use.

Reduction of phosphine oxide groups in PEPOs to phosphine

For the conversion of phosphine oxide groups to phosphine in PEPOs, phenylsilane was employed as a reducing agent as described earlier⁸ (Scheme 1). First, the polymer was dissolved in chlorobenzene at room temperature. Then, while stirring, phenylsilane was syringed slowly into the reaction flask and the mixture was heated to approximately 110 °C. After completion of the reaction, the polymer solution was precipitated into a 80:20 methanol/water mixture, filtered and dried. It was subsequently purified by redissolving in chloroform and reprecipitation into methanol, followed by vacuum-drying at 150 °C for 24 h. Using this method PEPOs were reduced to various PEPs (Scheme 2); **3a** and **3b** contain different ratios of phosphine oxide to phosphine (PO/P:).

Synthesis of poly(arylene ether phosphonium salt)s (PEP)s, **3**

The quaternization of phosphine groups in polymers **2a** and **2b** is illustrated in Scheme 2. The phosphine groups were readily converted to phosphonium using the alkyl halide **4**. Most of the reactions were initially carried out in chlorobenzene. However, as more phosphonium groups were formed the resulting polymers became less soluble in chlorobenzene and the solution turned cloudy. The addition of some methanol to the reaction mixture kept the solution homogeneous. The reaction of PEP with bromobenzene was carried



Scheme 2 Reduction of PEPOs to PEPs **3a** (R = Ph), **3b** (R = Me).

out in benzonitrile in the presence of nickel bromide according to the procedure described in the literature.¹¹

RESULTS AND DISCUSSION

The first step in development of phosphonium-based polymers was to synthesize the poly(arylene ether phosphine oxide)s, this synthesis was accomplished by reaction of the activated dihalide DFPPO and DFMPO with bisphenol-A using the known procedure for making poly(arylene ether)s (Scheme 1).⁶⁻¹⁰ Reduction of phosphine oxide groups in PEPOs was achieved with phenylsilane as a reducing agent⁸ (Scheme 2). In all cases, an excess of phenylsilane was used and the ratios of PEPO to phenylsilane were varied to investigate whether the reaction time could be decreased. In the case of PEPO **2a** it took more than 12 days at 110 °C to obtain nearly 100% reduction of phosphine oxide groups to phosphine; clearly, higher temperatures in a pressure vessel would reduce this time. However, **2b** underwent the same reaction to complete reduction in less than three days, presumably because of less steric hindrance around the phosphorus atom. All of the reactions were conducted under homogeneous conditions in chlorobenzene. Table 1 summarizes the reaction conditions and the results. The reduction was monitored by ³¹P NMR (see Table 2), by using the relative intensities of the peaks around 28 ppm and -7 ppm (referenced to phosphoric acid at 0.0 ppm), which correspond to phosphine oxide and phosphine, respectively, and this was the basis for the calculation of the percentage reaction conversion.

Quaternization of the phosphine groups to phosphonium salt was achieved using various alkyl

Table 1 Reduction of phosphine oxide to phosphine: reaction conditions and results

PEPO	PEPO/Silane	Reaction time (d)	Reduction (%)	Product (Conversion, %)
2a	3:6	2	30	3a (30)
2a	3:6	3	40	3a (40)
2a	3:6	5	57	3a (57)
2a	3:8	7	60	3a (60)
2a	3:8	12	94	3a (94)
2a	3:8	14	99	3a (99)
2b	3:8	3	100	3b (100)

^a percentage conversion of phosphine oxide to phosphine.

Table 2 ³¹P NMR spectral data of poly (arylene ether)s

Polymer ^b	Chemical shift ^a (ppm)		
	P=O	P:	P ⁺ X ⁻
2a	28.6		
3a (57)	28.3	-7.0	
3a (94)	29.2	-7.4	
4a (94)	31.8	—	22.8, 20.7 (8:1)
5a (94)	31.9	—	20.7
2b	30.1		
3b (100)		-28.6	
6a (94)	31.9	-7.5	22.5
7a (94)	31.4	—	22.3

^a Measured in mixture of chloroform-*d* and methanol, and reported relative to 85% H₃PO₄ (external, 0.0 ppm).

^b Values in parentheses are the percentage reduction.

or aryl halides (Scheme 2). Nearly quantitative conversion of phosphine to phosphonium was obtained according to ³¹P NMR. Chemical shifts of different phosphorus groups are listed in Table 2. The reaction of phosphine with iodomethane takes place at room temperature and it is so fast that the resulting polymer is precipitated as soon as the

iodomethane is added. The same reaction with propyl bromide requires at least a few hours before completion. In both cases methanol was added occasionally to the chlorobenzene solution in order to keep the polymers in solution. Generally, quaternization of polymer **3a** with alkyl halides was slower than that of polymer **3b**. Presumably this is because the phosphine groups in polymer **3b** are sterically less hindered than phosphine groups in polymer **3a**. Furthermore, the methyl group attached to phosphorus enhances the nucleophilicity of the phosphine, whereas the phenyl group decreases the nucleophilicity of the phosphine by delocalizing its non-bonding electrons. The reaction of benzy bromide with both **3a** and **3b** was also very fast and required only a few minutes at room temperature to reach completion. The completely aromatic phosphonium-based polymer was also prepared by reaction of **3a** with bromobenzene, using benzonitrile as solvent and nickel bromide as catalyst. The reaction was run at the reflux temperature of the solvent (*ca* 190 °C) for 3 h to obtain 90% conversion of phosphine to phosphonium salt, as shown in Table 3.

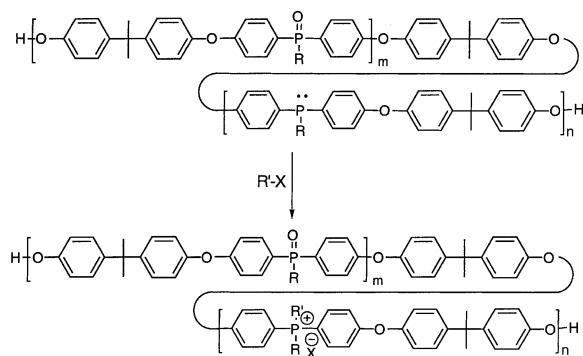
All the polyphosphonium salts could be solvent-

Table 3 Reaction conditions for quaternization of phosphine to phosphonium salt

Polymer ^a	R'-X	R	Reaction temp.(°C)	Solvent	Product ^b
3a (30)	nPrBr	Ph	65	PhCl/MeOH	4a (30)
3a (40)	nPrBr	Ph	65	PhCl/MeOH	4a (40)
3a (57)	nPrBr	Ph	65	PhCl/MeOH	4a (57)
3a (30)	MeI	Ph	25	PhCl/MeOH	5a (30)
3a (40)	MeI	Ph	25	PhCl/MeOH	5a (40)
3a (94)	nPrBr	Ph	65	PhCl/MeOH	4a (94)
3a (94)	MeI	Ph	25	PhCH ₃ /MeOH	5a (94)
3a (94)	PhBr	Ph	190	PhCN	6a (94)
3a (94)	PhCH ₂ Br	Ph	25	PhCl/MeOH	7a (94)
3b (100)	nPrBr	Me	65	PhCl/MeOH	4b (100)
3b (100)	MeI	Me	25	PhCl/MeOH	5b (100)

^a Values in parentheses are the percentage reduction.

^b Values in parentheses are the percentage reduction.



Scheme 3 Synthesis of PEPSs **4a,b**, **5a,b**, **6a**, **7a** from **3a,b**.

cast from a mixture of chloroform and methanol into films. Films of these polymers cast from dimethyl sulfoxide (DMSO) were transparent. Those polymers with a phosphonium content of 30–50% were only partially soluble in methanol. However, they became soluble in hot methanol and less soluble in chloroform when the salt content exceeded about 50%. Cloudiness of the methanolic solutions of the polymers at room temperature was eliminated by addition of chloroform. The films of polymers were not soluble in either cold or hot water. Some swelling was observed in samples with high salt content after prolonged stirring in hot water. Stable dispersion of the polymers (Scheme 3) **5a**, **6a** and **5b** in water was made possible by first dissolving the polymer in a small amount of methanol and then adding an excess of water to the methanolic solution. Ion-exchange reactions could readily be conducted to produce other counter-ions, including chromophores such as Methyl Orange or Methyl Red.¹⁰

CONCLUSIONS

A new class of main-chain polyphosphonium ionomers has been synthesized from poly(arylene ether phosphine oxide)s via reduction of phosphine

oxide groups to phosphine and subsequent quaternization of phosphine groups to afford phosphonium salts. Ion exchange can be used to prepare the new materials.¹⁰ Solubility of the polyphosphonium salts in methanol depends on the phosphonium content and can be varied from being partially to completely soluble. Polymers with high salt content are also water-dispersible. They may have some potential as water-dispersible sizings for carbon or glass fibers intended for polymer matrix composites, as well as novel polyelectrolytes.

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