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Interfacial synthesis of bisphenol A tetrachlorocyclotriphosphazene from bisphenol A and hexachlorocyclotriphosphazene



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Tiffany N. Thompson^{a,*}, Susan Ramos-Hunter^{a,b}, Jasmine Robertson^a, Natalie Y. Arnett^{a,b}

^a Fisk University, Department of Life and Physical Sciences, 1000 17th Ave. N., Nashville, TN 37208, USA ^b Vanderbilt University, Department of Chemistry, 7330 Stevenson Center, Station B 351822, Nashville, TN 37235, USA

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ABSTRACT

The effect of solvent purity on the synthesis and yield of bisphenol A tetrachlorocyclotriphosphazene (BATCCP) has not been described in the literature. The purpose of this research was to synthesize BATCCP hybrid monomers and to evaluate the effect of solvent purity on the BATCCP production. BATCCP monomers were prepared by an interfacial procedure in a water/toluene system as a function of time with the assistance of a phase transfer catalyst, tetraoctylammonium bromide. ¹H and ³¹P NMR confirmed the production of BATCCP monomer by the appearance of chemical shifts at 7.18 and 5.35 ppm in the ¹H NMR and 23.4 and 13.9 ppm in the ³¹P NMR, respectively. Distillation of the toluene, not suggested in previous reports of HCCP hybrid synthesis, resulted in an improvement of actual % yield to 40% and stability of the product throughout the 1440 min reaction as confirmed by MALDI, compared with an 11% actual yield at 15 min, decaying to 2% over a 1440 min reaction when the synthesis was performed with 'anhydrous toluene' as provided commercially without further distillation.

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Introduction

Sulfonated poly(arylene ether sulfone)s (PAES) are stable ionconducting polymers used in fuel cell and reverse osmosis membranes. Current PAES polymers are the product of co-polymerization of a sulfonated dichlorodiphenylsulfone (SDCDPS) and dichlorodiphenylsulfone (DCDPS) linked together with one of the varieties of bi-functional aryloxy groups, for example, bisphenol A (Bis A).¹⁻⁵ Higher degrees of sulfonation (above 50%) of PAES polymers lead to mechanical instability and excessive swelling of the fuel cell proton exchange membrane.^{6,7} The generic PAES backbones do not allow for crosslinking or other post-modifications that would permit enhancement of polymer properties for different applications. As a result, chemical or physical crosslinking ionomers have been widely pursued in an effort to overcome the problems with swelling and mechanical stability in these polymers.⁸ We postulate that one strategy for achieving variable PAES-based polymers would be to modify polymer synthesis so that bisphenol A or other aryl groups are introduced as a hybrid monomer with compounds that would introduce side chains for variable post-modifications. One such hybrid monomer would be bisphenol A conjugation with hexachlorocyclotriphosphazene (HCCP).

HCCP, a cyclic trimer of phosphonitrilic chloride, can form reactive cyclotriphosphazenes (CTPs) by nucleophilic substitution of one-to-six of its component chlorine groups. The present study reports the successful incorporation of the nucleophile bisphenol A into a hybrid monomer, bisphenol A tetrachlorocyclotriphosphazene (BATCCP). BATCCP monomers could serve as a pathway to the synthesis of BATCCP PAES-XX hybrid copolymers for use as proton exchange membranes in fuel cells.

Previous studies describing the synthesis of BATCCP have been reported.^{9,10} However, documentation to verify BATCCP formation was not given. Kumar⁹ reported the synthesis of nucleophilic arrangements of HCCP with a number of phenolic compounds, including bisphenols in toluene as a single phase reaction. Utilization of the same synthetic route in our laboratory yielded a mixture of unreacted Bis A, mono-substituted and di-substituted BATCCP products. Wu and Meng¹⁰ used a phase transfer catalyst (PTC) in an interfacial reaction to transport the catalyzed intermediate, phenyloxy, into an organic layer containing HCCP. Though NMR analysis was employed to monitor the formation of stereoisomers (geminal and nongeminal formations) during the reaction, no spectra were provided to confirm the formation of the putative products.

In the present study, BATCCP monomers were prepared interfacially using phase transfer catalysis in an immiscible solvent system of water and toluene. Analysis by NMR and MALDI confirmed the successful synthesis of the BATCCP hybrid monomer. During the course of our studies, we identified the importance of toluene solvent purity on both the rate and extent of product formation.



^{*} Corresponding author. Tel.: +1 615 329 8780; fax: +1 615 329 8577. *E-mail address*: tiffany.thompson064@gmail.com (T.N. Thompson).

Results and discussion

¹H NMR analysis of our synthetic product, shown in Figure 1, is consistent with the formation of a Bisphenol–HCCP adduct. The occurrence of the peak at 7.18 ppm (label 'f on spectrum) indicates the successful formation of a P–O bond between HCCP and Bis A to make BATCCP. The presence of the peak at 7.18 ppm arises due to the change in chemical environment of the proton on the aromatic ring closest to the oxygen ('f on BATCCP structure) from the loss of the phenolic proton to form the P–O bond with HCCP. The phenolic (O–H) proton at 5.35 ppm ('a' on spectrum and BATCCP structure) also indicated the successful synthesis of BATCCP. Peaks due to the presence of the phase transfer catalyst (TOABr) were observed at ~0.1, 0.9, 1.25, and 2.1 ppm.

³¹P NMR also supports the ¹H NMR data confirming the successful synthesis of BATCCP in the current study (Fig. 2). The triplet at 13.9 ppm is indicative of the phosphorous with two chlorine atoms attached ('a' on structure) while the doublet at 23.4 ppm ('b' on structure) is that of the phosphorous bonded to a chlorine atom and a bisphenol A molecule, as previously predicted. ³¹P NMR chemical shifts also were observed at 16.5 and 25.7 ppm, corresponding to predicted shifts for the mono-substituted side product, bisphenol A pentachlorocyclotriphosphazene (BAPCCP).

To optimize conditions to attain the highest yield of the desired BATCCP product, products achieved at 15, 120, 240, and 1440 min in reactions using distilled or undistilled toluene as solvent were analyzed by matrix-assisted laser desorption/ionization (MALDI). Figure 3 provides a MALDI spectrum for a 1440 min reaction using



Figure 1. ¹H NMR of BATCCP product. The letters indicate the chemical shifts corresponding to those in the BATCCP structure.



Figure 2. ³¹P NMR of BATCCP product. The letters indicate the chemical shifts corresponding to those in the BATCCP structure.



Figure 3. MALDI analysis of the products of the hybrid monomer interfacial synthetic reaction using distilled versus undistilled toluene as the organic phase. MALDI spectrum at 1440 min for synthesis with distilled toluene (a) and undistilled toluene (b). The predicted molecular weights for di-substituted BATCCP, the desired product, and mono-substituted BAPCCP are approximately 729 and 539 m/z, respectively. The product yield for each time point in distilled and undistilled toluene, using MALDI, is tabulated in (c). Calculations to determine the isolated yield (%), fractional (%), and actual BATCCP (%) yield can be found in the Supplementary data section.

distilled toluene (a) and undistilled toluene (b) as solvent; data from all time points assessed (tabulated in Fig. 3c) reveal that a higher % yield (40%) was obtained at 1440 min (24 h) for reactions conducted in distilled toluene. Since BAPCCP serves as the monosubstituted precursor for the desired di-substituted BATCCP product, the data in the presence of distilled toluene are as expected: as the BAPCCP decreases in fractional percent, that for BATCCP increases. In contrast, in undistilled toluene, the percent yield of BATCCP is trivial, due in large part to hydrolysis of the HCCP starting material and formation of HCCP dimers (cf. Fig. 3b), thus also explaining the unexpected BAPCCP precursor–BATCCP product relationship.

Conclusion

BATCCP was successfully synthesized by an interfacial synthesis through the use of a PTC. The product was confirmed through ¹H NMR, ³¹P NMR, and MALDI. The presence of the mono-substituted side product (BAPCCP) was also observed and was easily removed by purification. Preliminary research indicated that distilling the anhydrous toluene prior to the reaction has a large effect on the experimental outcome. Reactions carried out in distilled anhydrous toluene produced a higher actual % yield of BATCCP with a maximum yield of 40% after 1440 min of reaction.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013. 07.098.

References and notes

- 1. Xing, B.; Kerres, J. J. New Mater. Electrochem. Syst. 2006, 9, 51-60.
- Krishnan, N. N.; Kim, H. J.; Prasanna, M.; Cho, E.; Shin, E. M.; Lee, S. Y.; Oha, I. H.; Hong, S. A.; Lim, T. H. J. Power Sources 2006, 158, 1246–1250.
- Wang, F.; Hickner, M.; Kim, Y. S.; Zawodzinski, T. A.; McGrath, J. E. J. Membr. Sci. 2002, 197, 231–242.
- Harrison, W. LF.; Mecham, J. B.; Bhanu, M. H.; Kim, Y. S.; McGrath, J. E. J. Polym. Sci., Part A: Polym. Chem. 2003, 41, 2264–2276.
- Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E. Chem. Rev. 2004, 104, 4587–4612.
- Wang, F.; Hickner, M.; Kim, Y. S.; Zawodzinski, T. A.; McGrath, J. E. J. Membr. Sci. 2002, 197, 231.
- Kim, Y. S.; Hickner, M.; Dong, L.; Pivovar, B.; McGrath, J. E. J. Membr. Sci. 2004, 243, 317–326.
- Hong, Y. T.; Lee, C. H.; Park, H. S.; Min, K. A.; Kim, H. J.; Nam, S. Y.; Lee, Y. M. J. Power Sources 2008, 175, 724–731.
- 9. Kumar, D. Int. J. Adhes. Adhes. 1998, 18, 109-113.
- 10. Wu, H. S.; Meng, S. S. AIChE J. 1997, 43, 1309-1318.