

Proceedings

Synthesis of New Hyperbranched Phosphorus-Containing Polyesters Starting from Boltorn H20 †

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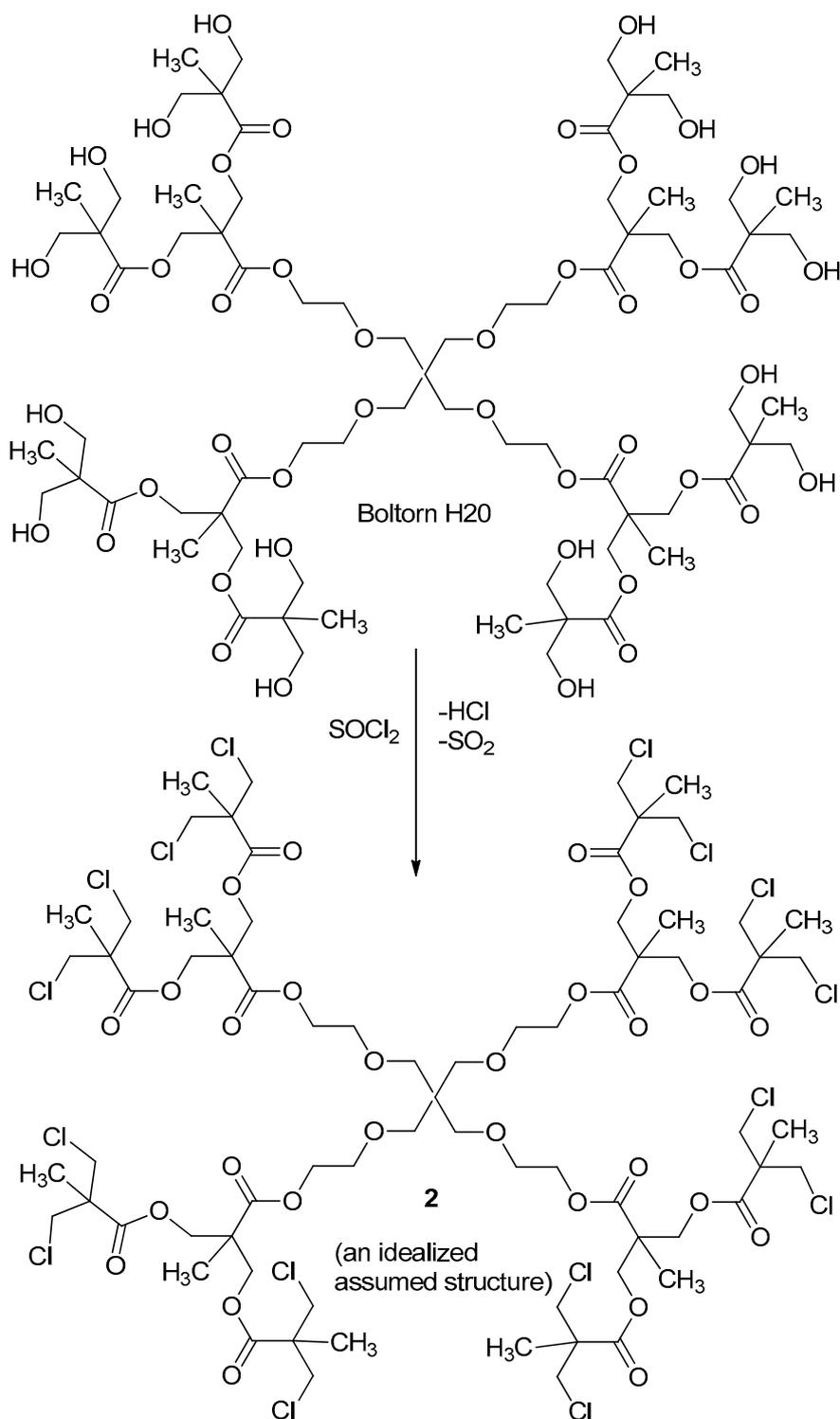
† Presented at the 22nd International Electronic Conference on Synthetic Organic Chemistry, 15 November–15 December 2018; Available Online: <https://sciforum.net/conference/ecsoc-22>.

Published: 16 November 2018

Abstract: Upon gentle treatment with SOCl_2 , hyperbranched polyester Boltorn H₂₀ afforded a mixture of terminal polychlorides. The latter react with an excess of triphenylphosphine in boiling toluene or with pyridine to give a mixture of polyesters with terminal triphenylphosphonium and pyridinium fragments, respectively.

Keywords: Boltorn H₂₀; hyperbranched polyesters; phosphonium chlorides

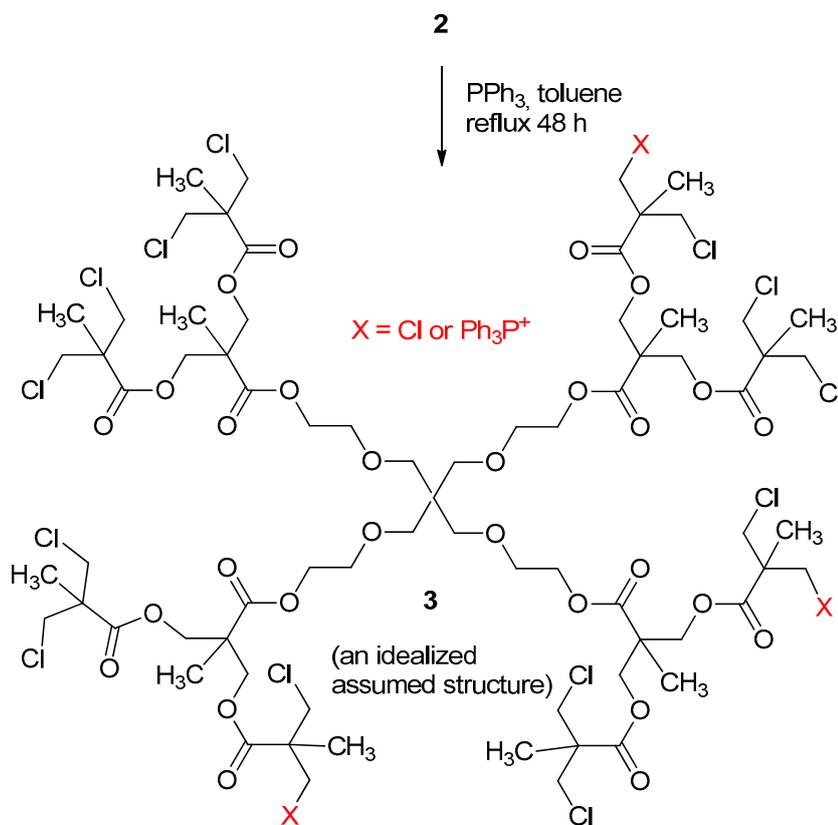
The wide application of bipolar membrane electrodialysis has aroused an interest in asymmetric bipolar membranes (ABMs) with cation-exchange and anion-exchange layers. A key feature of such membranes is that they partially desalt the solution not only to adjust the pH value. Such a bifunctionality of ABMs is responsible for low efficiency of ABMs in the production of strong acids and alkalis. Meanwhile, the bifunctionality of ABMs makes them promising for adjustment of pH of dilute electrolyte solutions. The main limitation of a more common use of ABM-based electrodialysis for pH adjustment processes in solutions is the high overvoltage across ABMs operating in the hydrogen and hydroxyl ion generation mode. To overcome these disadvantages and improve the electrochemical properties, a method of ABMs modification by introducing ionic polymers with catalytic activity in water dissociation into the bipolar region was proposed [1–7]. Hyperbranched polymers such as Boltorn H₂₀ are promising precursors for these catalysts. A significant advantage of hyperbranched polymers is that the number of reactive terminal groups in them is substantially larger than that in linear polymers. To make these polymers catalytically active in water dissociation, they have to be subjected to chemical functionalization. Here we propose the modification of Boltorn H₂₀ leading to the preparation of positively charged hyperbranched species having a catalytic activity in water dissociation. First, Boltorn H₂₀ was treated with SOCl_2 under mild conditions (either in 1,4-dioxane or in pure thionyl chloride) to give polychloride 2 (Scheme 1).



Scheme 1. The Reaction of Boltorn H20 with thionyl chloride.

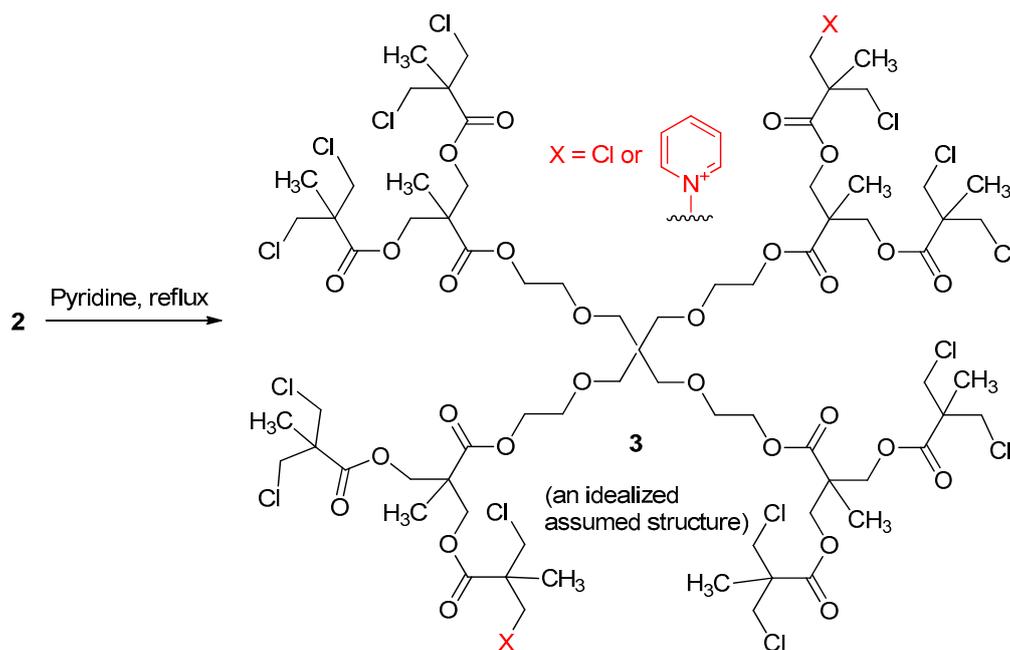
The reaction proceeds at 10–20 °C (external cooling) and is accompanied by evolution of HCl and SO₂; after 24 h the reaction was quenched with water to give polychloride 2 (an idealized assumed structure is presented in Scheme 1) as white precipitate insoluble in water, but soluble in nonpolar solvents. Next, to produce polycharged hyperbranched molecules, polychloride 2 was treated with (a) an excess of triphenyl phosphine in boiling toluene; and (b) with boiling pyridine. The reaction with PPh₃ resulted in the formation of clear solution which was evaporated to give colorless gummy residue. An excess of PPh₃ was removed by treatment with cold ether. The NMR ¹H analysis revealed that the product 3 is a mixture of phosphonium salts having different number of phosphonium groups (1–3) (Scheme 2). The reaction with pyridine resulted in the formation of

dark solution, which was evaporated under reduced pressure to give light-brown material, which was treated with cold ether to remove the traces of pyridine.



Scheme 2. Reaction of polychloride 2 with triphenyl phosphine.

The NMR ¹H spectrum of pyridinium product 4 (Scheme 3, Figure 1) revealed the presence of 1–2 pyridinium moieties per molecule, along with typical signals of Boltorn H20 core unit. The detailed analysis of NMR, IR and HRMS data will be reported elsewhere (Scheme 3).



Scheme 3. Reaction of polychloride 2 with pyridine.

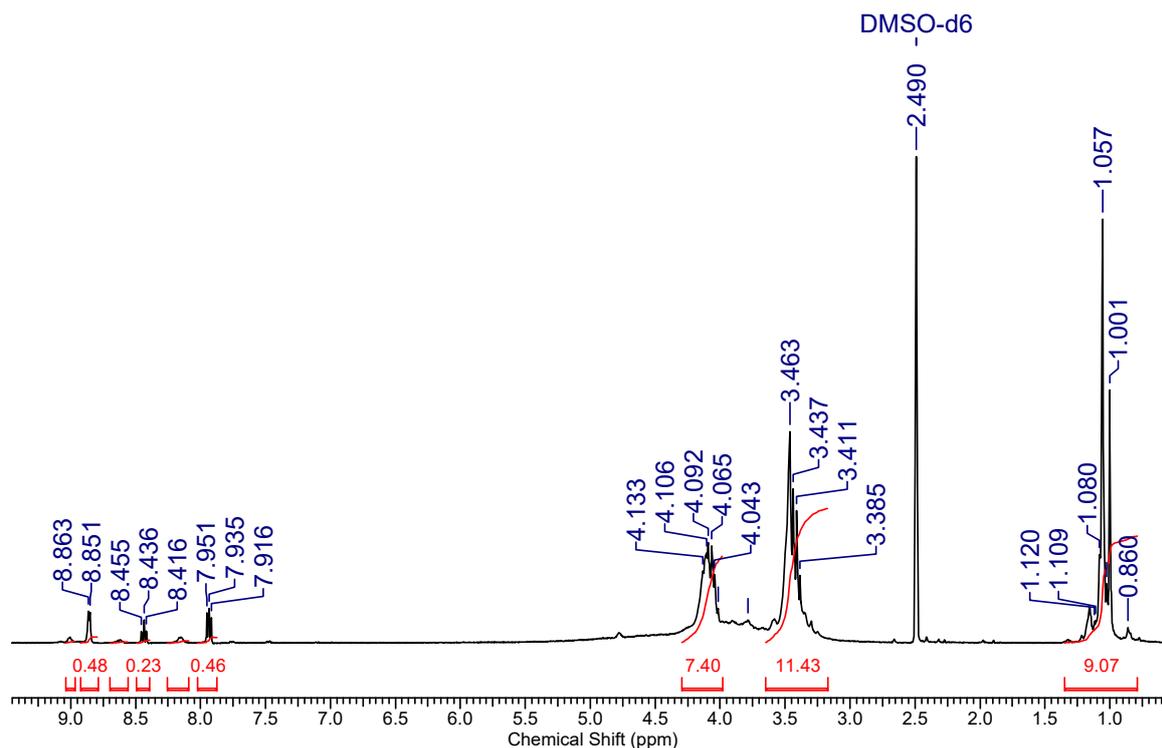


Figure 1. The NMR ^1H spectrum of pyridinium product **4** (400 MHz, DMSO- d_6).

Conclusions

We have developed an approach to the synthesis of hyperbranched polyesters bearing terminal triphenylphosphonium and pyridinium fragments, starting from commercially available hyperbranched polyester Boltorn H20. The prepared compounds are useful in the preparation of asymmetric bipolar membranes. The properties of membranes and detailed procedures will be reported elsewhere.

References

1. Kang, M.S.; Choi, Y.J.; Kim, S.H.; Moon, S.H. Enhancement of water splitting in bipolar membranes by optimized composite anion-exchange layer and alkali-treated polyacrylonitrile catalytic junction. *J. Membr. Sci.* **2004**, *229*, 137, doi:10.1016/j.memsci.2003.10.021.
2. Xu, T.W.; Yang, W.H. Fundamental studies on a novel series of bipolar membranes prepared from poly(2,6-dimethyl-1,4-phenylene oxide) (PPO): I. Effect of anion exchange layers on I–V curves of bipolar membranes. *J. Membr. Sci.* **2004**, *238*, 123, doi:10.1016/j.memsci.2004.03.028.
3. Xu, T.W.; Fu, R.Q.; Yang, W.H.; Xue, Y.H. Fundamental studies on a novel series of bipolar membranes prepared from poly(2,6-dimethyl-1,4-phenylene oxide) (PPO): II. Effect of functional group type of anion-exchange layers on I–V curves of bipolar membranes. *J. Membr. Sci.* **2006**, *279*, 282, doi:10.1016/j.memsci.2005.12.016.
4. Mel'nikov, S.S.; Zabolotskii, V.I.; Shel'deshov, N.V. Electrochemical properties of asymmetric bipolar membranes. *Kondens. Sredy Mezhfaz. Granitsy* **2010**, *12*, 143. (In Russian)
5. Zabolotskii, V.I.; Sheldeshov, N.V.; Melnikov, S.S. Effect of cation-exchange layer thickness on electrochemical and transport characteristics of bipolar membranes. *J. Appl. Electrochem.* **2013**, *43*, 1117, doi:10.1007/s10800-013-0560-3.
6. Wang, Q.; Wu, B.; Jiang, C.; Wang, Y.; Xu, T. Improving the water dissociation efficiency in a bipolar membrane with amino-functionalized MIL-101. *J. Membr. Sci.* **2017**, *524*, 370, doi:10.1016/j.memsci.2016.11.056.

7. Utin, S.V.; Loza, S.A.; Bespalov, A.V.; Zabolotsky, V.I. Effect of functionalization and the nature of ionogenic groups of hyperbranched polymers on the electrochemical characteristics of asymmetric bipolar membranes. *Petrol. Chem.* **2018**, *58*, 137–144, doi:10.1134/S0965544118020068.



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