Synthesis of aromatic polyethers by Scholl reaction

X. Synthesis and cation-radical polymerization of 1,5-bis(1-naphthoxy)-3-oxapentane*

Virgil Percec**, James H. Wang, and Lisha Yu

Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH-44106-2699, USA

ABSTRACT

This paper describes the synthesis and cation-radical polymerization of 1,5-bis(1-naphthoxy)-3-oxapentane. This monomer contains a flexible diethylene oxide unit between two 1-naphthalene rings. The FT-IR analysis of the resulted polymer indicates that it contains 1,4-disubstituted naphthalene structural units, i.e. 4,4'-disubstituted-1,1'-binaphthalene units. The polymer is crystalline with a melting point of 236 °C.

INTRODUCTION

Functional aromatic polyethers such as polyether sulfones and polyether ketones are conventionally synthesized by variants of aromatic nucleophilic substitution or aromatic electrophilic substitution reactions. Two novel approaches to the synthesis of these functional aromatic polyethers have been demonstrated by cation-radical polymerization of bisaryloxy derivatives by Scholl reaction and by the homocoupling of aryl halides by Ni catalyzed reactions.

The cation-radical polymerization of 4,4'-bis(phenoxy)diphenyl sulfone, 4,4'-bis(phenylthio)diphenyl sulfone, and 4,4'-bis(phenoxy)diphenyl sulfone substituted with various electron-donating groups leads to polyether sulfones of only low molecular weight. This is caused by the low polymerizability of these monomers. The polymerization of 1,5-bis(phenoxypentanes substituted with methyl groups is also accompanied by proton transfer reactions from the benzylic groups. The cation-radical polymerization of bis(1-naphthoxy) monomers leads to high molecular weight polymers when the starting monomers are 4,4'-bis(1-naphthoxy)diphenyl sulfone, bis(1-naphthoxy)benzophenone, bis(1-naphthoxy)diphenyl sulfone substituted with methyl groups is also accompanied by proton transfer reactions from the benzylic groups. The bis(1-naphthoxy) monomers investigated so far are summarized in Scheme 1.

This communication presents some preliminary results on the synthesis and the cation-radical polymerization of the first monomer containing a flexible diethylene oxide central unit, i.e. 1,5-bis(1-naphthoxy)-3-oxapentane.

EXPERIMENTAL

Materials

1-Naphthol (3) (99%, Aldrich), FeCl₃ (anhydrous, Aldrich), Bis(2-chloroethyl) ether (4, 99%, Aldrich), and K₂CO₃ (Fisher) were used as received. Dimethyl sulfoxide (DMSO, Fisher) was distilled from CaO. Nitrobenzene (PhNO₂, Fisher) was distilled from CaH₂ under nitrogen. Other solvents were used as received.


**To whom offprint requests should be sent
Scheme 1. Structure of bis(1-naphthoxy) and bis(2-naphthoxy) monomers polymerized by cation-radical reactions.