N-alkoxy pyridinium ion terminated polytetrahydrofurans. Synthesis and their use in photoinitiated block copolymerization

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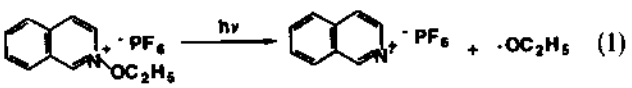
Living polytetrahydrofuran was terminated with pyridinium or isoquinolinium N-oxide to yield polymers with the corresponding end groups. Direct and sensitized irradiation of these photoactive polytetrahydrofurans produced alkoxyl radicals at both chain ends capable of initiating the radical polymerization of methyl methacrylate. In this way, triblock copolymers were formed. The block copolymer composition was determined with the aid of g.p.c. and optical and ^{1}H n.m.r. spectroscopy.

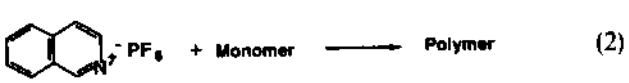
(Keywords: living cationic polymerization; tetrahydrofuran; pyridinium ions)

INTRODUCTION

Living polymerization allows the preparation of various well-defined polymers with functional end groups. It has been shown that cyclic ethers such as tetrahydrofuran (THF) can be polymerized without chain transfer and termination reactions under closely controlled conditions[1-3]. The oxonium group of the living chain can react with nucleophiles and thus gives rise to a variety of functional groups[4-6]. Pyridinium salts are generally prepared by reacting N-oxides with triethyloxonium salts. Since the oxonium ion is the end group of living THF chains, N-alkoxy pyridinium ion terminated polymers can be obtained by quenching the living ends of the polymer with N-oxides. It has been shown that certain N-alkoxy pyridinium and N-alkoxy isoquinolinium ions are capable of acting as photoinitiators for the cationic polymerization[7-9]. A possible mechanism for the initiation of cationic polymerization applies to the photolytic generation of radical cations and ethoxyl radicals. This is illustrated for the case of the N-ethoxy isoquinolinium ion by reactions (1) and (2):

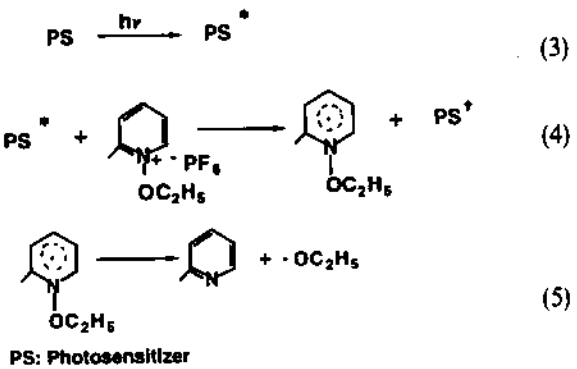


(1)



(2)

The decomposition of pyridinium ions also can be induced indirectly via the reaction with electronically excited sensitizers (PS).



PS: Photosensitizer

The alkoxyl radicals so generated can initiate the free radical polymerization of appropriate monomers[10]. Therefore, it seemed feasible to use polytetrahydrofurans (PTHFs), terminated by N-alkoxy pyridinium ions, as polymeric photoinitiators for the polymerization of monomers such as methyl methacrylate (MMA) that readily polymerize by a free radical mechanism. As will be shown below, block copolymers of THF and MMA, i.e. of monomers of quite different chemical nature, can be prepared by this method.

In the text, the polymers terminated by N-alkoxy-2-methyl pyridinium, N-alkoxy-4-phenyl pyridinium or N-alkoxy isoquinolinium ions are denoted by PTHF-MP, PTHF-PP and PTHF-IQ, respectively.

EXPERIMENTAL

Materials

THF was dried over potassium hydroxide, distilled over sodium wire and finally distilled over sodium/benzophenone ketyl prior to use. MMA (Aldrich) was passed through a column containing basic alumina (Type Brockmann 1) and distilled over CaH_2 *in vacuo*

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