

Preparation of azo functional poly(isobutyl vinyl ether) oligomers and block copolymers via combination of living cationic and condensation polymerization

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This paper reports the synthesis and characterization of azo functional poly(isobutyl vinyl ether) oligomers and block copolymers containing poly(isobutyl vinyl ether) and oligoesterdiol segments. Isobutyl vinyl ether was polymerized using a trifluoromethanesulfonic acid/tetrahydrothiophene initiating system in dichloromethane at -30°C , and quantitatively terminated with labile azo compounds to give poly(isobutyl vinyl ether) with well-defined molecular weight and end-groups. Also, diblock copolymers with poly(isobutyl vinyl ether) and oligoesterdiol segments were synthesized by termination of living, cationically polymerized isobutyl vinyl ether with oligoesterdiol.

(Keywords: poly(isobutyl vinyl ether); labile azo groups; oligoesterdiols)

INTRODUCTION

Living cationic polymerization affords control over the molecular weight, molecular weight distribution and end-groups of the resulting polymer. Additionally, the highly reactive chain-ends of living cationic polymers can be used for the synthesis of telechelics, block copolymers and other functional polymers.

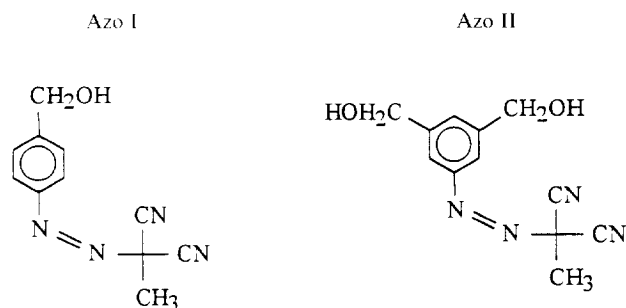
In 1984, Higashimura *et al.*¹ reported the first example of a truly living cationic polymerization of an alkyl vinyl ether initiated by an HI/I_2 system. There are now a number of initiating systems for the living cationic polymerization of alkyl vinyl ethers².

Recently, Webster *et al.* and Lin and Matyjaszewski⁴ have reported a new initiating system for the synthesis of living alkyl vinyl ether polymers. In this system, a mixture of a strong protonic acid (trifluoromethanesulfonic acid) and a Lewis base (sulfide), which stabilizes the active chain-ends, affords the living polymerization. Goethals *et al.*⁵ have used this initiating system in order to obtain macromonomers by end capping of living polymers with tertiary amines or alcohols.

Alkyl vinyl ether block copolymers have also been prepared by other methods². One method involves sequential living polymerization and is a simple way for the synthesis of block copolymers. The first monomer is polymerized to give a living polymer upon which, without quenching, the second monomer is polymerized^{6–8}. Another method involves polymerization from a macroinitiator in which the functional group of the initiator is introduced into a living, cationically polymerized poly(alkyl vinyl ether)⁹. Accordingly, Nuyken *et al.*^{10,11} have prepared poly(isobutyl vinyl ether) with labile azo groups available for free radical vinyl copolymerization. The method of polymer

coupling has rarely been used to obtain poly(alkyl vinyl ether) block copolymers, in contrast to the frequent use of sequential living polymerization for the synthesis of living alkyl vinyl ethers. However, Rife and coworkers^{12,13} have prepared diblock copolymers containing poly(methyl methacrylate) and poly(alkyl vinyl ether) segments using a combination of living cationic and living group transfer polymerization techniques.

We now report the coupling reactions of living poly(isobutyl vinyl ether) and oligoesterdiols initiated by the trifluoromethanesulfonic acid (triflic acid)/tetrahydrothiophene system that afford ABA-type block copolymers. Furthermore, the living poly(isobutyl vinyl ether) was quenched with the hydroxy functional labile azo compounds azo I and azo II.



EXPERIMENTAL

Materials

Isobutyl vinyl ether (IBVE) (Aldrich) was dried overnight with calcium hydride and distilled under