

SYNTHETIC ROUTES TO BLOCK COPOLYMERIZATION BY CHANGING MECHANISM FROM CATIONIC POLYMERIZATION TO FREE RADICAL POLYMERIZATION

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Abstract: Polymers containing thermolabile groups were synthesized by various cationic polymerization initiation mechanisms, namely; oxo-carbenium, promoted cationic and activated monomer polymerization. These polymers used in a subsequent blocking step in which azo groups were decomposed and converted into initiating centres from which blocks were grown by means of free radical polymerization. This procedure was applied to specific systems in which cationic polymerizable monomers are tetrahydrofuran (THF), cyclohexene oxide (CHO) and epichlorohydrin (ECH), respectively, and the free radical polymerizable monomer is styrene (St).

Introduction

There has been an enormous interest in the synthesis of block copolymers due to their unique and novel properties which are a consequence of their molecular structure. Although various methods have been known for a long time, living polymerization techniques are preferred since they allow the synthesis of block copolymers with well defined structures in terms of molecular weight control and narrow molecular weight distributions. However, these techniques are limited to special monomers and exclude monomers that polymerize by other mechanisms. Much of the recent research effort (Refs.1-3) has been directed towards the utility of different polymerization techniques thus giving access to a wide range of monomer combinations which offer unusual properties.

Although block copolymerization by radical techniques leads to a variety of products as a result of transfer and termination reactions, it is extensively employed due to a wide choice of monomer combinations and low sensitivity towards impurities. This paper demonstrates new routes to block copolymers by combining cationic polymerization and free radical polymerization via functional initiator approach. In these processes, initiating cations are formed at the both ends of suitable azoinitiators and the azo group that remained in the polymer chain is decomposed for the subsequent free radical polymerization (scheme 1).