

Polymer Communication

# Synthesis of block copolymers by transformation of photosensitized cationic polymerization to stable free radical polymerization

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## Abstract

Anthracene-photosensitized cationic polymerization of cyclohexene oxide at  $\lambda = 350$  nm in conjunction with onium salts, namely *N*-ethoxy-2-methyl pyridinium hexafluorophosphate ( $\text{EMP}^+\text{PF}_6^-$ ) or diphenyliodonium hexafluorophosphate ( $\text{Ph}_2\text{I}^+\text{PF}_6^-$ ), in the presence of a stable radical, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), yielded polymers with alkoxyamine terminal groups. These polymers were found to be efficient initiators for stable free radical polymerization (SFRP) of styrene. IR,  $^1\text{H-NMR}$  spectral analysis and GPC studies of the obtained polymers show that block copolymers are readily formed as a result of combination of photosensitized cationic and stable free radical polymerization mechanisms. © 1999 Elsevier Science Ltd. All rights reserved.

**Keywords:** Transformation reactions; Photosensitized cationic polymerization; Stable free radical polymerization

## 1. Introduction

The various methods have been proposed and used for the synthesis of block copolymers [1]. Among them the transformation approach is an elegant way to cover a wide range of monomer combinations [2,3]. Transformation reactions involve synthesis in which two (or more) mutually exclusive polymerization mechanisms are sequentially combined. The transformation approach, comprises different propagating species and allows multiple combination of monomers. In this approach monomer 1 is polymerized by a mechanism 'A' to produce a polymer with a functional group F that is capable of initiating polymerization by a different mode/mechanism 'B' (Scheme 1).

Many examples concerning the use of transformation reactions in block copolymers were reported by us and others [1,3].

*N*-alkoxy pyridinium salts are effective initiators for the cationic polymerization of cyclic ethers such as cyclohexene oxide and vinyl ethers such as *n*-butyl vinyl ether [4]. Their photoactivity can be tuned to a broad wavelength range by the use of free radical sources [5], charge transfer complexes [6] and photosensitizers [7].

Photosensitized cationic polymerization attracted particular interest since the triggering of the initiation may be extended to much longer wavelengths, where pyridinium

salts are transparent and photosensitizers such as anthracene, perylene and phenothiazines absorb the light. The electron transfer mechanism has been postulated as demonstrated for the case of anthracene photosensitizer [7] (Scheme 2)

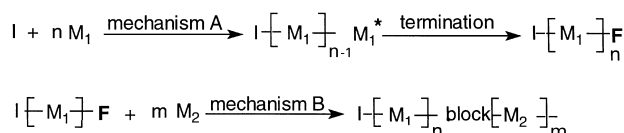
Controlled "stable free radical polymerization" (SFRP) has recently been a study of increasing interest [8,9]. This type polymerization can be realized through reversible deactivation of growing radicals by stable radical such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (Scheme 3).

In the present work, a block copolymer of cyclohexene oxide (CHO) and styrene (St) was prepared by sequential polymerization of photosensitized cationic polymerization and stable free radical polymerization.

## 2. Experimental

### 2.1. Materials

Dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), styrene (St) and cyclohexene



Scheme 1. Transformation reactions.

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