

# Block Copolymers by Combination of Cationic and Radical Routes: 6. Synthesis of Tetrahydrofuran-Vinyl Block Copolymers\*

İ. Ersin SERHATLI, Gürkan HIZAL, Yusuf YAĞCI

*İstanbul Technical University*

*Arts-Sciences Faculty Department of Chemistry İstanbul-TURKEY*

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Polytetrahydrofuran with a thermo-sensitive group was prepared by reacting 4,4'-azo bis (4-cyanopentanoyl chloride) with  $AgPF_6$  in the presence of tetrahydrofuran. These polymers were used to induce the radical polymerization of various vinyl monomers through the thermal decomposition of the azo group, resulting in the formation of poly (tetrahydrofuran-b-vinyl) copolymers.

## Introduction

Block copolymers that contain poly (tetrahydrofuran) (PTHF) segments are of interest.<sup>1</sup>

Incorporation of soft PTHF blocks into conventional vinyl polymers should lead to polymers with the desired physical properties. It is well known that tetrahydrofuran (THF) is a nucleophilic monomer and polymerizes by the cationic mechanism. Cationic polymerization is limited to certain types of vinyl monomers and excludes the possibility of preparing block copolymer of THF with other monomers that polymerize by other mechanisms. Additionally, contamination of homopolymers can not be prevented since chain transfer reactions dominate cationic polymerization of vinyl monomers. Richard<sup>2,3</sup> proposed an elegant method that allows combination of THF with monomers. In this approach, polystyrene, prepared anionically, is terminally functionalized, isolated and subsequently used to initiate the polymerization of THF cationically to form block copolymers. Similarly, Abadie et al<sup>4</sup> described block copolymerization of THF with vinyl monomers by transformation of radical centers into cationic centers. Previously, we presented a new approach of preparing block copolymers by cation to radical<sup>5,6</sup> and reverse<sup>7,8</sup> transformation polymerization. This approach is based on the use of a bifunctional low-molecular weight initiator containing acid-chloride end groups and an azo-group. The most effective usage of this initiator was made by reacting acid chloride groups with non-nucleophilic silver salts in the presence of THF and subsequent thermal decomposition of the azo-group in the presence of styrene (St).

\* For part 5 of this series, see Polymer 31, 1803 (1990)