Block copolymers by combination of cationic and radical routes: 4. Cationic polymerization of tetrahydrofuran initiated by difunctional azo-oxocarbenium initiator*

Gürkan Hızal and Yusuf Yağcı†
Technical University of Istanbul, Department of Chemistry, Maslak, Istanbul 80626, Turkey
(Received 10 June 1988; accepted 7 October 1988)

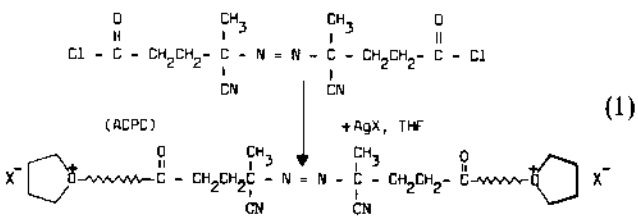
The kinetics of the bulk polymerization of tetrahydrofuran initiated by 4,4-azobis(4-cyanopentanoyl chloride) in conjunction with silver salts have been studied at −20, 0 and 10°C. Propagation rate constants increase with increasing temperature ($k_p = 4.7 \times 10^{-4}$ at −20°C, 3.7×10^{-3} at 0°C and 1.2×10^{-2} l mol^{-1} s^{-1} at 10°C) and an Arrhenius plot gives an activation energy of 57.6 kJ mol^{-1}. The enthalpy and entropy changes were estimated to be $\Delta H_p = -24$ kJ mol^{-1} and $\Delta S_p^\circ = -86.7$ J K^{-1} mol^{-1} respectively. Spectroscopic and degradation studies showed that polymers obtained via this initiation method contained one azo linkage per macromolecule chain.

(Keywords: block copolymer; cationic polymerization; azo-oxocarbenium initiator; azo linkage)

INTRODUCTION

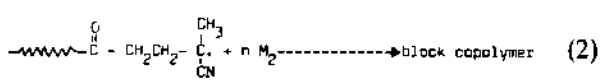
There has been an enormous amount of interest in block copolymers, owing to their use as thermoplastics, elastomers, adhesives, etc. The synthesis, characterization and properties of block copolymers have recently been reviewed by several authors[1–3]. Transformation reactions extend the range of possible monomer combinations in block copolymers[3].

Recently, Yağcı presented[4–6] a new conceptual approach to preparing block copolymers by cation-to-radical and reverse transformation polymerization. The method involves a two-stage procedure. First, synthesis of a polytetrahydrofuran (PTHF) containing one azo linkage in the main chain by the use of a difunctional azo-oxocarbenium initiator:



(1)

and then decomposition of the azo linkage, which gives rise to the formation of block copolymers in the presence of a monomer susceptible to radical polymerization:



(2)

A different sequence of this procedure may also be employed[6].

A common feature of both methods is that the overall structure of the block copolymers depends on the mode of termination of the free-radical polymerization step. Moreover, the polymerization conditions of both cationic and free-radical steps are expected to govern the chain lengths of PTHF and polyvinyl sequences of block copolymers, respectively. Therefore, we have investigated kinetic and mechanistic details of the cationic polymerization of tetrahydrofuran (THF) initiated by a so-called azo-oxocarbenium initiator together with the thermal decomposition of the azo-linked PTHF obtained. Detailed investigations of the free-radical polymerization step by means of azo-linked PTHF will be the subject of future publications.

EXPERIMENTAL

Materials

THF was purified by conventional drying and distillation procedures. $AgSbF_6$, $AgBF_4$ and 4,4-azobis-(cyanopentanoic acid) (Fluka) were used without further purification. The corresponding diacid chloride (ACPC) solution was prepared according to a previously described procedure[7].

Polymerization procedures

Polymerizations were carried out under a dry nitrogen atmosphere. Appropriate stock solutions of silver salts ($AgSbF_6$ or $AgBF_4$) and ACPC in THF were prepared by distillation of THF in a high-vacuum system. The polymerizations were initiated by mixing the two solutions, by means of a syringe, in a reaction vessel sealed under

* Dedicated to Professor A. C. Aydoğan on the occasion of his retirement

† To whom correspondence should be addressed

0032-3861/89/040722-04$03.00