

Block copolymers by combination of cationic and radical routes: 5. Polymerization of styrene initiated by 4,4'-azobis(4-cyanopentanoyl chloride)*

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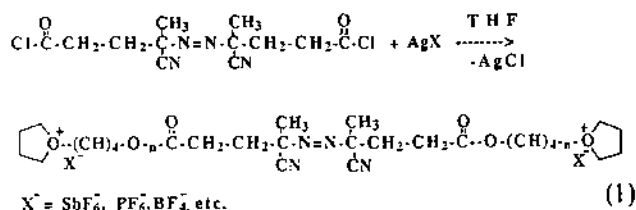
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The kinetics of the polymerization of styrene initiated by 4,4'-azobis(4-cyanopentanoyl chloride) (ACPC) was investigated in bulk and in benzene solution at 60°C. It was found that the overall rate of polymerization is proportional to the 0.48 power of the initiator concentration. The chain transfer-to-initiator and chain transfer-to-solvent constants were estimated to be $C_1=0.41$ and $C_5=1.9 \times 10^{-4}$, respectively. Polymerization of styrene initiated by ACPC yields polystyrene with an acyl chloride terminal group at each end. Polymerization of tetrahydrofuran initiated by acyl chloride-terminated polystyrene in conjunction with AgSbF_6 provided the formation of a block copolymer.

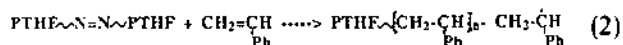
(Keywords: block copolymer; cationic polymerization; free-radical polymerization; chain transfer reaction)

INTRODUCTION

We have previously established¹⁻³ that the synthesis of block copolymers by the combination of cationic and radical routes may be accomplished by a two-step procedure. First, 4,4'-azobis(4-cyanopentanoyl chloride) (ACPC) when reacted with a silver salt having low nucleophilic ions in the presence of tetrahydrofuran (THF) produces a diacyl cation and polymerization at both ends by an addition mechanism:



Detailed kinetic and mechanistic investigations⁴ revealed that the resultant polytetrahydrofuran (PTHF) contains one ($-\text{N}=\text{N}-$) group in the main chain. Thermal decomposition of the azo linkage produces two polymeric radicals per chain, which gives rise to the formation of block copolymers in the presence of a monomer susceptible to free-radical polymerization (e.g. styrene):



This type of block copolymer greatly depends on the kinetic behaviour of the monomer employed in the second step of the procedure.

A different sequence of the same procedure may also be used⁵. Polymerization of tetrahydrofuran initiated by polymers endowed with acyl chloride groups in

conjunction with a silver salt provided the formation of block copolymers. One way⁵ to produce polystyrene with acyl chloride end-groups is to react the living polystyrene with excess phosgene at 70°C. Dimerization of initial polystyrene molecules during phosgenation and termination by impurities contained in the phosgene were a deterrent to the use of this method. Alternatively, free-radical polymerization of styrene initiated by 4,4'-azobis(4-cyanopentanoic acid) (ACPA) and subsequent treatment of these polymers with PCl_5 yielded two acyl chloride end-groups. This method suffers from the difficulty in treating a small amount of functional groups present in the long chain with PCl_5 and successive leaching for the removal of phosphorus oxychloride from the polymer. Therefore, it seemed suitable to use ACPC as a free-radical initiator for the polymerization of vinyl monomers, in order to obtain, directly, acyl chloride-terminated polymers having appropriate functionality for the subsequent cationic step leading to the formation of block copolymers. A similar approach⁶ was applied to prepare block copolymers by reacting acyl chloride-terminated polystyrene with diols. The present work reports the kinetic studies of polymerization of styrene initiated by ACPC together with block copolymerization by means of the polystyrene obtained.

EXPERIMENTAL

Materials

Styrene and THF were used as free-radical and cationically polymerizable monomers, respectively, and were freed from inhibitors by conventional drying and distillation procedures. Benzene, n-hexane, methylene chloride and petroleum ether (40-60) were dried and distilled before use. AgSbF_6 (Aldrich), ACPA (Fluka) and PCl_5 (Merck) were used as-received. The corresponding diacid chloride ACPC was prepared according to a procedure described elsewhere⁷.

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