Synthesis, Decomposition, and Initiator Properties of Macroazonitriles for the Preparation of Polymers with Crown Ether Units

UMIT TUNCA and YUSUF YAGCI, *Istanbul Technical University, Department of Chemistry, Maslak, Istanbul 80626, Turkey*

Synopsis

Macroazonitriles containing crown ether moieties and various amounts of $-N=N-$ units in the main chain were prepared by solution polycondensation between *cis*-diamino dibenzo-18-crown-6 (DADC) and adipoyl chloride (AC) or terephtaloyl chloride (TPC) with the addition of 4,4′-azobis(4-cyanopentanoyl chloride) (ACPC). Decomposition of the azo linkage present in the polyamides, obtained by using TPC, were studied by DSC. The rate constants and activation energies for the decomposition were determined and a small effect of terephtaloyl group on the rate was observed. The kinetics of the polymerization of styrene by the poly(azoamide), obtained from ACPC and DADC were investigated in DMSO.

INTRODUCTION

Recently, the binding of ions by crown ethers has been a subject of interest with emphasis on the relationship between binding and structure.[1,2] Polymers bearing crown ether groups strongly bind ions of various size. Even ions whose ionic diameter exceeds the size of crown ether cavity are bound[3-5] through the cooperative effect of two crown units. To combine crown ether structures with polymers, most approaches have been through condensation reactions.[6-8] In these reactions, derivatives of crown ethers were used with two functional groups. On the other hand, Smid and co-workers[9] synthesized 4′-vinyl benzo crown ether to form polymers having pendant crown ether groups.

Macroazonitriles prepared by condensation[10,11] or by cationic[12] and anionic insertion[13] polymerization, enable the synthesis of block copolymers with different types of monomers.

Recently, we have synthesized a macroazoinitiator for the synthesis of polymers with crown ether units by solution[10] and interfacial polycondensation reaction.[11] The latter provided complexation of the crown ether moiety before the polymer was synthesized, and the crown ether complex probably acted also as a phase transfer catalyst between water and organic phase. The resulting polyamide is a useful initiator for free radical polymerizations to yield block copolymers.

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 28, 1721–1733 (1990)
 CCC 0887-624X/90/071721-13$04.00